I. Studies on the Coordination of Bis-hydroxybenzamido Chelating Ligations to Chromium, Iron, and Osmium

II. A Survey of the Organometallic Chemistry of Osmium Tetraoxide

Thesis by

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Last and assuredly not least I would like to thank my parents, family, and friends from Ohio who have kept me from getting too homesick through their calls, letters, visits, and tasty care packages.

G.H.S.

ABSTRACT

The coordination chemistry of chromium, iron, and osmium with bis-hydroxybenzamido chelating ligands was investigated. Two types of complexes were obtained on reacting $CrCl_3 \cdot 6H_2O$ with 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-ethane ($(H)_4$CHBA-Et). A neutral dimeric complex, in which two chelates bridge two metal centers, was discovered and characterized by *X*-ray crystallography. This is the first molecule in which both forms of monodentate organic amide coordination (*i.e.*, *O*-bound and *N*-bound coordination) have been found. The *N*-bound amide was shown to be a better σ-donor. This is the first well-characterized example of *N*-coordination to chromium(III).

A second complex, which is a precursor to the neutral dimer, has not been fully characterized. It may also be dimeric. Similar complexes, with different bis-hydroxybenzamido ligands, have been examined. Iron(III) species, synthesized from these ligands and $FeCl_3$, appear to be analogous to the latter chromium(III) compounds.

X-ray crystallographic studies have complemented investigations into the coordination chemistry of these bis-hydroxybenzamido ligands with several transition metals. In addition to the dimeric chromium(III) complex, in which the ligand bridges two metal centers, many osmium(IV) complexes were found with the bis-hydroxybenzamido ligands coordinated to one metal center as a planar tetradentate tetraanion. These structures exhibited the first examples of bonds between osmium(IV) and an *N*-coordinated organic amide ligand and a phenoxide ligand. One such complex, a μ-oxo dimer, was found with potassium ions in unusually low coordination environments (*i.e.*, four- and five-coordinate). Oxidation of *trans*-Os(CHBA-Et)$(py)_2$ subsequently resulted in crystals of a new complex with a hydroxy and a methoxy group on the ethylene unit bridging the amide nitrogen atoms of the chelated ligand. The bond distances and angles for this molecule are very similar to those of its precursor, *trans*-Os(CHBA-Et)$(py)_2$. The ligand, $(H)_4$CHBA-Et, was found to cocrystallize with pyridinium

chloride. This structure has provided a benchmark for comparison with complexed chelates; few significant differences were observed.

The fusion of 2,3-bis(2-hydroxy-benzamido)-2,3-butane with $(NH_4)_2OsCl_6$ (T>300°C) resulted in the formation of an osmium(IV)-imidazoline complex.

Also examined was the organometallic chemistry of osmium tetraoxide. Oxidation of low valent carbonyl complexes with the quinuclidine adduct of osmium tetraoxide resulted in attack of both the low valent metal and a carbonyl ligand with the formation of μ-CO_2 mixed-valent complexes. The surprising stability of this new type of CO_2 complex is kinetic in origin as demonstrated by the chemistry of a series of compounds. Decomposition with loss of CO_2 was observed for more labile metal complexes. In the absence of nitrogenous bases, oxidation of $Ru(CO)_3(PPh_3)_2$ with osmium tetraoxide resulted in the formation of what is believed to be a tetranuclear complex. The low valent metal center and a coordinated carbonyl ligand were oxidized.

One other mode of reactivity was discovered. Oxidative addition of osmium tetraoxide to $Pt(PPh_3)_2(C_2H_4)$ displaced the ethylene ligand with the formation of a μ-oxo bridged tetranuclear complex. These and other potential modes of OsO_4 reactivity with organometallic and inorganic complexes are discussed.

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ABBREVIATIONS FOR SPECTROSCOPIC DATA

Infrared Spectroscopy (IR):

br	broad
mb	medium and broad
ms	medium and sharp
s	strong
sb	strong and broad
sh	sharp
ss	strong and sharp

Nuclear Magnetic Resonance Spectroscopy (NMR):

d	doublet
m	multiplet
s	singlet

Chapter 1

Studies on the Coordination of Bis-hydroxybenzamido Chelating Ligations to Chromium, Iron, and Osmium.

Introduction

Studies on the oxidation of organic and inorganic compounds have been an area of considerable interest since the nineteenth century.[1] Today, oxidation chemistry encompasses a wide spectrum of research ranging from electrochemistry and redox reactions of metal ions to stoichiometric and catalytic oxidative transformations of organic functional groups. Our work has focused on two aspects of oxidation chemistry:

- investigating ligand systems that have the potential to stabilize transition metals in the higher oxidation states, to ultimately design improved oxidants for organic synthesis, and
- characterizing the reactivity of classical oxidants, such as osmium tetraoxide, with low valent organometallic complexes.

The development of new oxidants for organic synthesis and the modification of known reagents has traditionally been a rather empirical process due to the complex nature of most metal-based organic oxidations.[2] However, at our present level of understanding other strategies are possible. In many metal-oxidant/organic-substrate systems, the participation of more than one active species in the overall oxidation has been documented.[3] This generally results in poor chemoselectivity due to the differing reactivity of each active oxidant. The challenge is to learn how to control these specific reactions — to be able to transform multicomponent oxidations into single component oxidations, which are usually very chemoselective.[4]

The oxidation of secondary alcohols with chromic acid is a well-studied example.[5] The mechanism of this reaction is now thought to involve four main stages:

$$Cr(VI) + R_2CHOH \longrightarrow Cr(IV) + R_2CO \qquad \text{(Stage 1)}$$

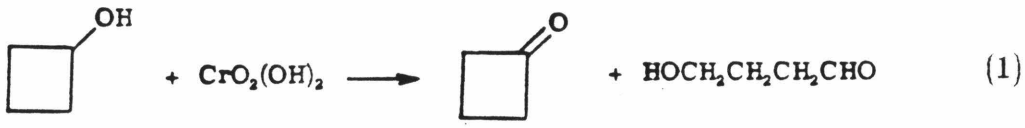
$$2Cr(IV) + 2R_2CHOH \longrightarrow 2Cr(III) + 2[R_2COH]^{\bullet} \qquad \text{(Stage 2)}$$

$$2Cr(VI) + 2[R_2COH]^{\bullet} \longrightarrow 2Cr(V) + 2R_2CO \qquad \text{(Stage 3)}$$

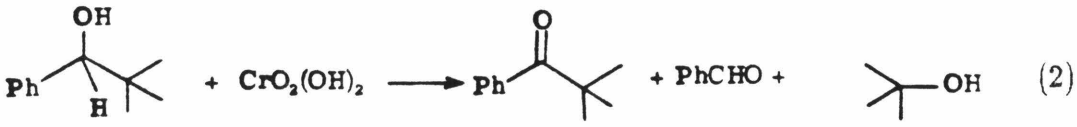
$$2Cr(V) \longrightarrow Cr(VI) + Cr(IV) \qquad \text{(Stage 4).}$$

Here the initial reaction (Stage 1) is complicated by the additional reactivity of a transient chromium(IV) species. The organic radicals formed in Stage 2 of this oxidation often undergo rearrangement reactions. Thus, when these rearrangements are faster that oxidation of the radical species, additional products are observed. As predicted by the stoichiometry, up to 66% of the alcohol can be converted into products other than the ketone.

The effect of multicomponent oxidants on the chemoselectivity was illustrated by a classic study. To probe the multicomponent nature of the chromium(VI) oxidation of secondary alcohols, Roček carried out several experiments with cyclobutanol and phenyl-*t*-butylcarbinol in which he was able to quench either the oxidations by chromium(IV) or by chromium(VI). Under the usual conditions, the chromic acid oxidations of these alcohols resulted in the formation of several products, cyclobutanone and 4-hydroxybutanal or pivalophenone, benzaldehyde, and *t*-butanol, respectively.



(1)



(2)

Addition of vanadyl perchlorate, which has been shown to rapidly reduce chromium(VI) to chromium(V) and (more slowly) chromium(V) to chromium(IV),[6] allowed the organic oxidation to occur solely with chromium(IV); in the chromic acid/cyclobutanol system, the only oxidation product isolated was the cleavage product, 4-hydroxybutanal. Conversely, addition of cerium(III) to the chromic acid/alcohol system quenched the reactivity of chromium(IV) by a rapid disproportionation reaction of chromium(IV) to chromium(VI) and chromium(III).[7] In

the presence of cerium ion phenyl-*t*-butylcarbinol was oxidized with the formation of only a minimal amount (5%) of the cleavage products, benzaldehyde and *t*-butanol. The lesson from this system is that while the overall oxidations by chromic acid exhibit poor selectivity, each chromium component appears to be very chemoselective. The multiple products observed, therefore, result from the superposition of a number of chemoselective reactions, each producing a specific oxidized compound.

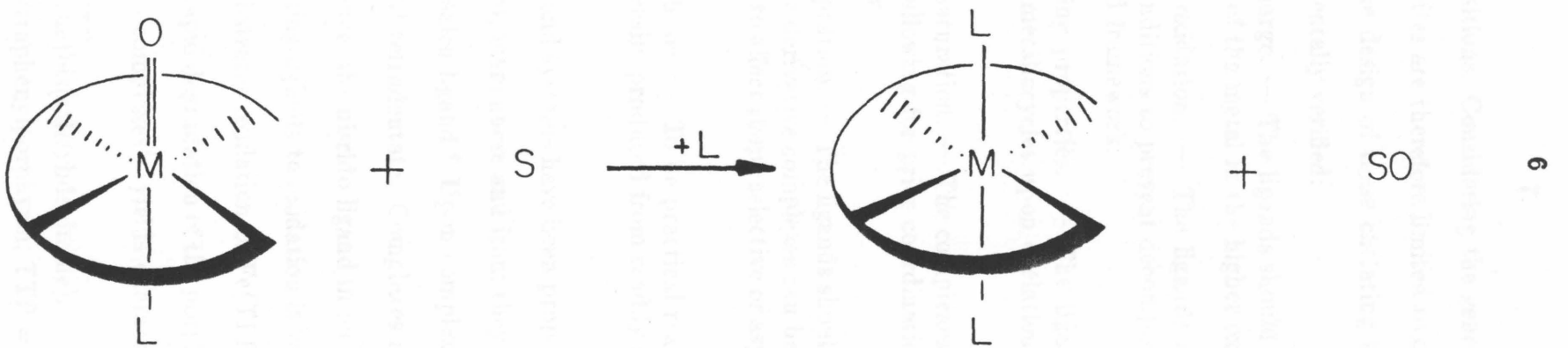
We believe the way to produce chemoselective metal-oxo oxidizing agents is to design systems in which it is possible to control oxidation state changes at the metal. Our approach has been to provide a well-defined coordination sphere at the transition metal center. To accomplish this goal, studies have been initiated utilizing chelating ligands that have the potential to:

- form high oxidized and highly oxidizing transition metal complexes, and
- form intermediate oxidation state reduced species, designed to be stable to further reduction.

Shown in Scheme 1.1 is a schematic reaction for an oxo transfer oxidation involving the proposed transition metal complexes of a tetradentate tetraanion. The chelating ligand serves to stabilize the higher valent species by providing a coordination sphere of negatively charged contact atoms and it preserves the integrity of the inorganic compounds due to the chelate effect. The main advantage is that the oxidation is limited to one oxidizing species, since the redox reactions are matched, *i.e.*, a straightforward net transfer of two electrons. The suppression of side reactions should lead to improved yields.[4] The possibility exists for both stoichiometric reactions or catalytic regeneration of the high valent complex using co-oxidants, *e.g.*, iodosylbenzene,[8] which might make reagents of this kind attractive for both small-scale and large-scale applications.

Suitable chelating ligands, *i.e.*, those that stabilize high valent transition metals, are rare.[9] Most known high oxidation state compounds contain hard monodentate donors such as F^-, Cl^-, Br^-, O^{-2}, N^{-3}, and O_2^{-2}. New multidentate ligands will most likely have to mimic them, incorporating hard donor

Scheme 1.1. Proposed organic oxo transfer reaction involving potential high valent mono-oxo complexes.


O
M
L
+
S
+L
L
M
L
+
SO

atoms in the contact positions. Considering the general geometric requirements of chelates, the binding sites are therefore limited to oxygen and nitrogen atoms. Proposed features for the design of these chelating ligands are outlined below; some have been experimentally verified:

1. High negative charge. — The ligands should be multianionic to counter the high positive charge of the metal in the higher oxidation states.

2. Insensitivity to oxidation. — The ligands must be able to withstand the strongly oxidizing conditions to prevent decomposition of the complexes and degradation of the ligand framework.

3. Superior chelating properties. — The ligands should form favorable (five- or six-membered) metallacycles upon chelation and should be resilient to hydrolysis.

4. Coordinative unsaturation. — The complexes should have available sites for chemistry to occur, allowing for prior coordination of the organic substrate to the metal, if necessary.

5. Potential for adaptation. — The ligands should be easily modified so that the oxidizing power of the derivative complexes can be attenuated. Incorporation of steric bulk or chirality to affect shape selective or asymmetric oxidations should also be possible.

6. Economical syntheses. — To be practical reagents for organic synthesis, these ligands should be easily produced from readily available starting materials in high yield.

Several chelating ligand systems have been proposed and/or shown to stabilize high valent chromium, manganese and iron; they include porphyrin and corrole derivatives and the salen ligand.* Upon complexation these planar chelates are di- and trianionic and tetradentate. Complexes are known to accommodate the oxo and, in one instance, the nitrido ligand in an axial site (Figure 1.1). The sensitivity of these chelating ligands to oxidation is variable. For instance, in the absence of oxidizable substrates oxidation of Fe(TPP)Cl and Fe(TTP)Cl† with iodosylbenzene leads to rapid degradation of the porphyrin.[10] Oxidation of Cr(II) and Cr(III) porphyrinato complexes[11] yields characterizable Cr(IV) and Cr(V)

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* salen = *N*,*N*'-(ethylene)bis(salicylidenimine).

† TPP = dianion of tetraphenylporphyrin; TTP = dianion of tetra-*o*-tolylporphyrin.

complexes; however, their catalytic activity with iodosylbenzene in oxidations of organic substates (*e.g.*, alkenes) is shortlived. In general, these ligands are not well protected from oxidative degradation.

The characterization of high valent transition metal complexes has been difficult. Structures have often been proposed by implication from their reactivity, *i.e.*, studies on the oxidation of alkanes, alkenes, arenes, etc. Such characterizations are far from being totally satisfactory. Controversy and uncertainty surround most of these studies due, in part, to limited spectroscopic techniques and to the fact that few high valent complexes have been isolated. Many of these complexes are stable only at reduced temperature (−80°C) and/or in solution. This is especially true for purported iron(IV)- and iron(V)-oxo complexes. (TmTP)FeOOFe(TmTP)‡ is known to form a new complex, {FeO(TmTP)(MeIm)}$_x$, upon addition of a stoichiometric amount of *N*-methylimidazole (MeIm) at −80°C.[12] Magnetic susceptibility measurements and its paramagnetic behavior suggest it is a monomeric iron(IV)-oxo complex, *viz.*, FeO(TmTP)(MeIm), but its full acceptance as an oxo complex must await definitive spectroscopic evidence. There are examples of well-characterized compounds. A polymeric complex, *catena*-(μ-oxo)(hemiporphyrazinato)iron(IV), with alternating μ-oxo ligands between the iron centers has recently been characterized by *X*-ray crystallography.[13] Characterized manganese compounds include: Mn(TPP)(OMe)$_2$, {Mn(TPP)X}$_2$O (X = N_3^-, OCN^-), MnN(T*p*MPP), and two as yet not definitively characterized complexes incorporating iodosyl ligands: {Mn(TPP)Y(OIPh)}$_2$O (Y = Cl^-, Br^-), and Mn(TPP)(OI(OAc)Ph)$_2$.*[14]

Compounds of high valent chromium have been isolated as well; all are oxo compounds. Treatment of Cr(TPP)Cl with iodosylbenzene produces the chromium(V) compound, CrO(TPP)Cl, which decomposes on standing to CrO(TPP); this molecule has been structurally characterized.[11] A similar corrole

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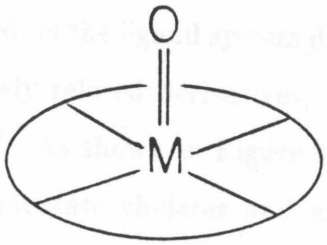
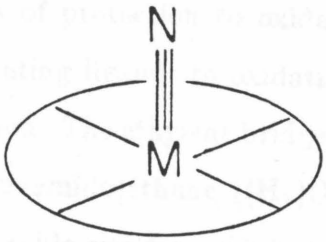
‡ TmTP = dianion of *meso*-tetra-*m*-tolylporphyrin.

* TPP = dianion of tetraphenylporphyrin; T*p*MPP = dianion of *p*-methoxyphenylporphyrin.

Figure 1.1. Schematically illustrated known high valent complexes.


O
M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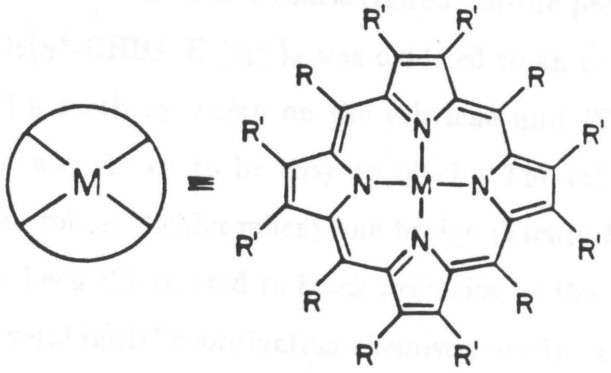
M
≡
R'
R
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N
M
N

derivative, CrO(tetmc),[§] is prepared by eluting the chromium(III) complex over silica gel (aerial oxidation).[15] Recently, it was reported that $[Cr(salen)(H_2O)_2]PF_6$ would react with iodosylbenzene producing $[CrO(salen)]PF_6$,[16] which also has been structurally characterized. This complex as well as many of the porphyrinato complexes have been shown to epoxidize alkenes.

Our studies have focused on the ligand system derived from 1,2-bis(2-hydroxybenzamido)ethane and closely related derivatives, which meets many of the requirements outlined above.[17] As shown in Figure 1.2, these compounds are potentially tetraanionic, tetradentate chelates and upon coordination they form five- or six-membered chelate rings to the metal. The oxidative sensitivity of the ethylene unit, bridging the two hydroxybenzamido moieties (Figure 1.2a,c), was recognized at the onset. However, an argument existed that the tetradentate tetraanion would be such a powerful donor that the oxidizing properties of the derived complexes would be small. Consequently, it was decided to find out by experimentation what kinds of protection to oxidation were indeed necessary. The sensitivity of these chelating ligands to oxidation was found to be variable depending on the derivatization. The ethylene bridge in the prototype ligand, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane ((H_4)CHBA-Et, Figure 1.2c), was recently identified as a vulnerable site for oxidative degradation.[18] Chemical or electrochemical oxidation of *trans*-Os(η^4-CHBA-Et)$(py)_2$ resulted in the eventual cleavage of the carbon-carbon bond of the ethylene unit. Many intermediates in the overall degradation scheme were isolated and characterized. In the presence of methanol and water, *trans*-Os(η^4-CHBA-Et)$(py)_2$ was oxidized to an unusual compound with a hydroxy and a methoxy group on the ethylene unit (Figure 1.3). This unwanted reactivity was shown to be easy to block. The ethylene bridge was replaced by the more robust dichlorophenylene bridge (Figure 1.2d). The phenol rings have routinely been chlorinated to block oxidation at the *ortho* and *para* positions. However, several initial coordination chemistry studies of low

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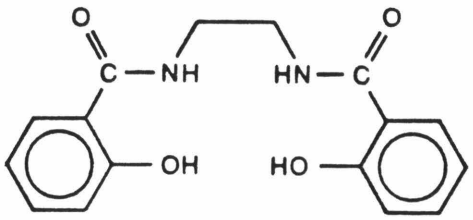
[§] tetmc = the trianion of 7,8,12,13-tetraethyl-2,3,17,18-tetramethylcorrole.

Figure 1.2. Potentially tetraanionic tetradentate planar bis-hydroxybenzamido chelates used in these studies.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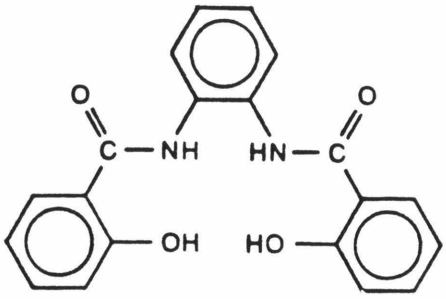
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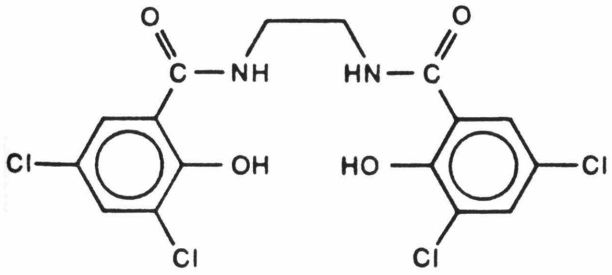
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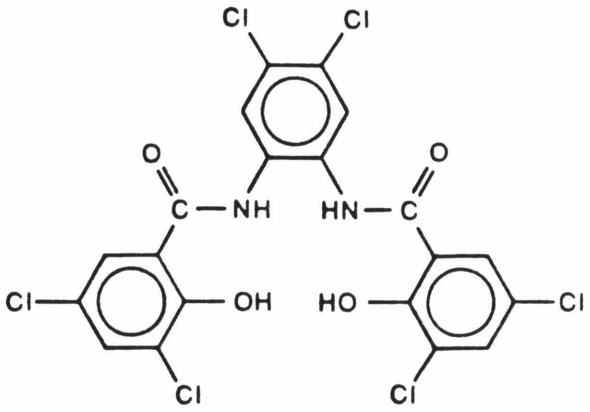
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Cl
Cl

d

valent metals were performed using unchlorinated derivatives. These investigations have provided a foundation for the development of related transition metal systems including an alcohol oxidation catalyst.[18]

An important feature of 1,2-bis(2-hydroxybenzamido)ethane and its derivatives is the incorporation of the amide functional group into the central binding sites. Peptides and related compounds, containing the amide group, have been studied as models of metal-protein binding, especially with the late transition metals.[19] Interestingly, the +III oxidation state of copper and nickel can be stabilized in these systems. Margerum has found that the electrochemical potential E° of the couple $Cu^{III,II}$ decreases as the number of (*N*-bound) deprotonated amides coordinated to the metal increases (Table 1.1).[20] The E° values range from 0.98 V (*vs.* NHE) for one deprotonated *N*-bound amide to 0.55 V for three coordinated amide groups. Birker has structurally characterized the stable complex, tetra-n-butylammonium *o*-phenylene-bis(biuretato)cuperate(III)·chloroform,[21] and along with Bour and Steggerda has characterized a number of biuret complexes: K[M-(biuret)$_2$] (M = Cu(III), Ni(III), Co(III))[22]; here the coordination is via the "amide" nitrogen atoms. A cobalt(IV) complex containing *N*-bound organic amide ligands, *trans*-Co(η^4-CHBA-DCBz)(4-*t*-Bupy)$_2$,[†] has recently been characterized by our group.[23] The stabilization of the higher oxidation states is expected to be a a general characteristic of *N*-coordinated amide groups for other metals such as chromium, manganese, and iron.

There have been few investigations reported in the literature concerning *N*-bound coordination of the amide functional group to the earlier transition metals, *i.e.*, to the triads of scandium to iron. Sigel and Martin believe this is due to the failure of these transition metal ions to substitute for the amide hydrogen.[24] Due to the high basicity of the deprotonated amide nitrogen atom in aqueous solution ($pK_a = 15$), metal ion hydrolysis often occurs before the amide coordination step. However, in some metal/chelating ligand systems, metal ion substitution at an

[†] CHBA-DCBz = tetraanion of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene.

Figure 1.3. ORTEP view of *trans*-Os(η^4-CHBA-HMEt)(py)$_2$.

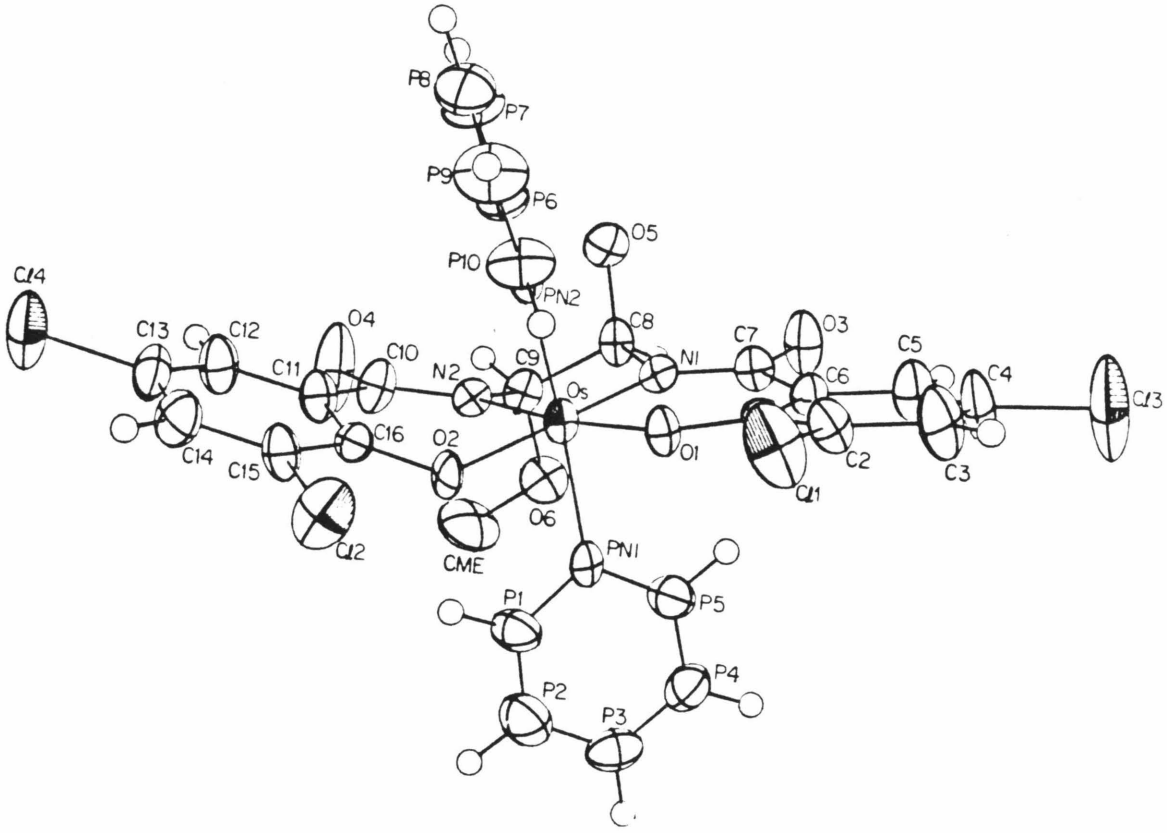
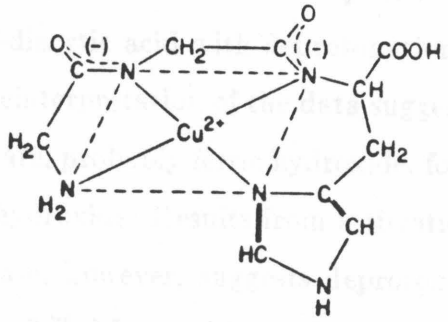

P8
P7
P9
P6
O5
P10
PN2
C14
C13
C12
O4
C8
C7
O3
C5
C10
C11
N2
C9
N1
C6
C4
C13
Os
C16
O2
O1
C14
C15
C2
C3
Cl1
Cl2
O6
CME
PN1
P1
P5
P4
P2
P3

Table 1.1. The dependence of coordinating groups on E° of $Cu^{II,III}$ couples.

Cu(III)-Peptide	pH	$E°(V)^a$
Cu(H_{-2}glycylglycyl-L-histidine)	7.5	0.98
Cu(H_{-2}triglycine)	7.7	0.92
Cu(H_{-2}diglycinamide)(OH)	9.2	0.89
Cu(H_{-3}triglycinamide)	9.5	0.64
Cu(H_{-3}tetraglycine)]$^{-1}$	9.3	0.63
Cu(H_{-4}*N*-formyltetraglycine)]$^{-2}$	11.5	0.55

[a] $Cu^{II,III}$ couples are reported *vs.* NHE and determined by cyclic voltammetry with a carbon paste working electrode. $[CuL]_T = 5 \times 10^{-4}$M, $\mu = 0.1$ M $NaClO_4$, 25°C.



Cu(H_{-2}glycylglycyl-L-histidine)

amide group is possible when prior coordination of other binding sites allows for favorable five- and six-membered chelate rings to be formed.* Ions such as Pd^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+} generally exhibit pK_a values for the peptide hydrogen displacement reaction (equation 3) of 2, 4, 8, and 10, respectively.

$$M^{2+} + R'CONRH \rightleftharpoons H^{+} + [R'CONR\text{–}M]^{1+} \qquad (3)$$

According to Sigel and Martin, the pK_a values for the earlier transition metal ions are prohibitively high. However, few, if any, of these investigations have been conducted in organic solvents or under aprotic conditions which may drastically affect the observed results. The role of the "chelate effect" is also an important factor, though its influence is hard to define, making comparisons between various metal-ligand systems difficult.

Exceptions have been found. Compounds of osmium and the ligands 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane and 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene have been characterized, several by *X*-ray structural analysis; *trans*-Os(η^4-CHBA-Et)(py)$_2$ is shown in Figure 1.4.[18] In all cases the osmium is located in the central site bound to the deprotonated phenolic oxygen atoms and the deprotonated amide nitrogen atoms. Other reports of *N*-coordination to the earlier transition metals have appeared in the literature. Martell proposed that aqueous ferric ion complexed to ethylenediamine-*N,N'*-di(acetylglycine)-*N,N'*-diacetic acid with deprotonation of both amide hydrogen atoms at high pH.[25] Reinterpretation of the data suggests this is incorrect due to the fact that a precipitate, probably ferric hydroxide, formed during the titration with aqueous sodium hydroxide. Results from a titration of aqueous ferrous ion and bleomycin with base, however, suggests deprotonation of an amide group does occur near pH = 6.[26] Most other studies of these early transition metals with compounds containing the organic amide and related functional groups have found only *O*-bound complexes such as *trans*-Cr(biuret)$_2$Cl$_2$ (Figure 1.5).[27]

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* *N*-coordination of organic amides has been found only when the amide group has been part of a larger multidentate ligand.

However, several dimeric chromium(II) complexes in which the bidentate amide group bridges the two metal centers (Figure 1.6) have been found.[28]

Our interest in developing new oxidants for organic synthesis has inspired the initial goals of this project: to investigate the coordination chemistry of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane (and other derivatives) with many transition metals (chromium, iron, and osmium in this work) and eventually explore the oxidation chemistry of the higher valent complexes. In designing routes to these compounds we have considered the previous work with chelating ligands, described above, and we have looked to other characterized compounds of chromium, iron, and osmium as well. Table 1.2 summarizes most of the known compounds involving other ligands which contain carbon and hydrogen for these metals in the higher valences.

Figure 1.4. ORTEP view of *trans*-Os(η^4-CHBA-Et)(py)$_2$.

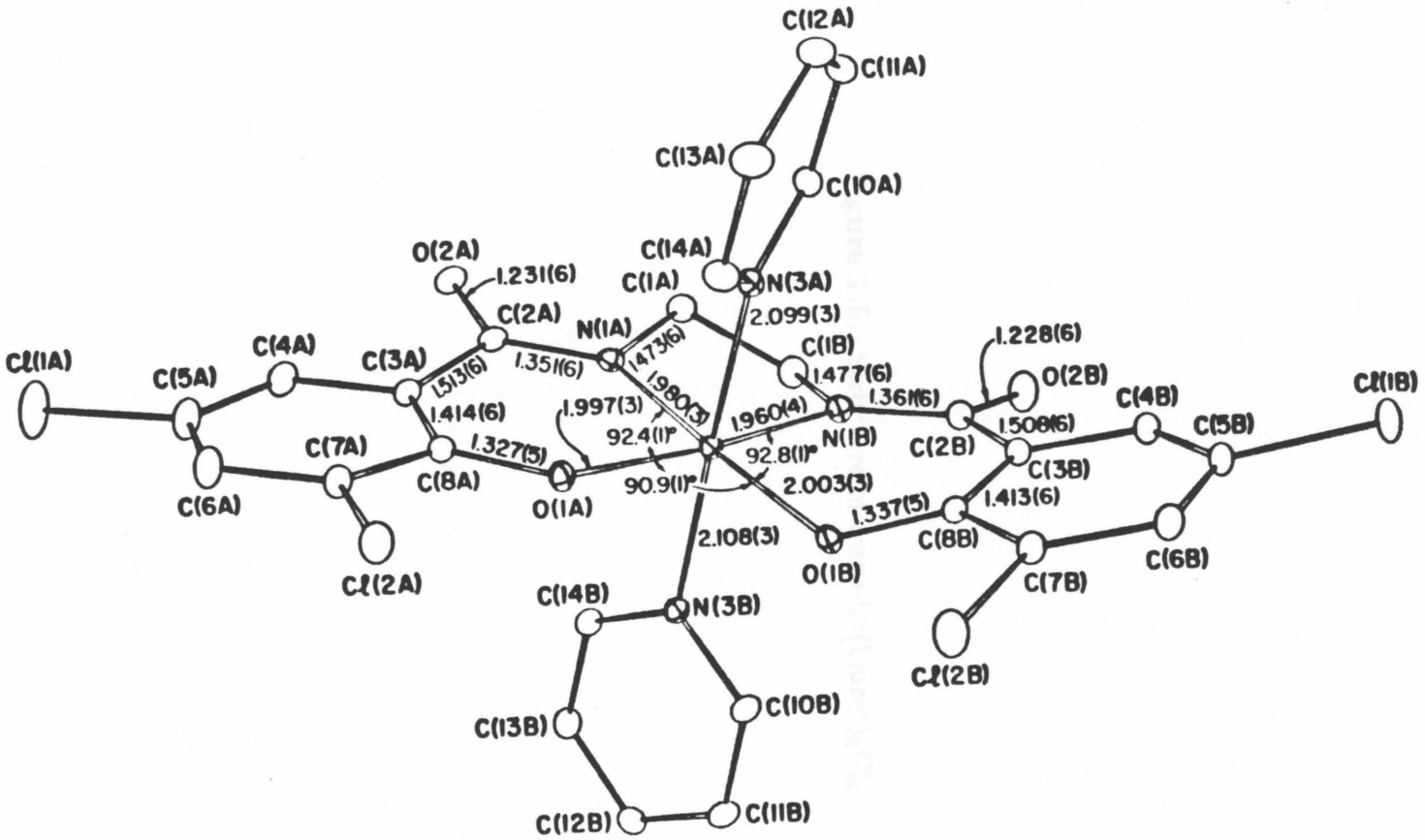

C(12A)
C(11A)
C(13A)
C(10A)
O(2A)
1.231(6)
C(14A)
C(1A)
N(3A)
2.099(3)
C(2A)
N(1A)
1.473(6)
C(1B)
1.228(6)
Cl(1A)
C(4A)
C(3A)
1.513(6)
1.351(6)
1.477(6)
O(2B)
Cl(1B)
C(5A)
1.414(6)
1.997(3)
1.980(3)
1.960(4)
1.361(6)
C(4B)
C(5B)
C(7A)
1.327(5)
92.4(1)°
92.8(1)°
N(1B)
C(2B)
1.508(6)
C(3B)
C(6A)
C(8A)
O(1A)
90.9(1)°
2.003(3)
1.337(5)
1.413(6)
C(8B)
C(6B)
Cl(2A)
2.108(3)
O(1B)
C(7B)
C(14B)
N(3B)
Cl(2B)
C(10B)
C(13B)
C(12B)
C(11B)

Figure 1.5. Structure of *trans*-$Cr(biuret)_2Cl_2$.

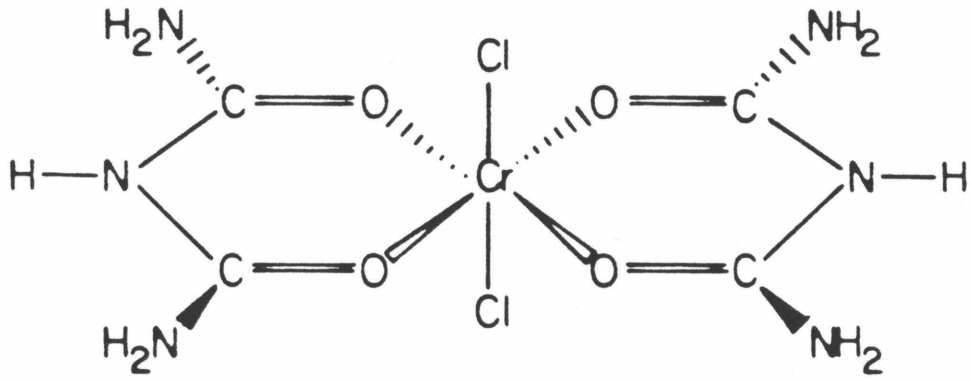

H2N
NH2
Cl
O
O
C
C
H
N
N
H
Cr
C
C
O
O
O
O
Cl
H2N
NH2

Figure 1.6. Dimeric chromium(II) bridging amido complexes.

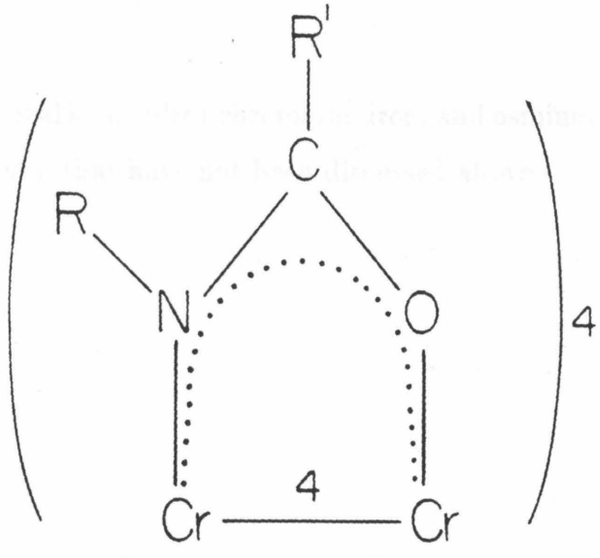

R'
C
R
N
O
4
4
Cr
Cr

Table 1.2. Several high valent chromium, iron, and osmium complexes, involving organic fragments, that have not been discussed above.

High valent chromium complexes:

CrR_4 [a]

$Cr(OR)_4$ [b]

$Cr(NR_2)_4$ [c]

$CrO(O_2CCR_2O)_2$ [d]

$CrO_2(O\text{-}t\text{-}Bu)_2$ [e]

$CrO_2(O_2CCH_3)_2$ [f]

$CrO_2\left(OX(C_6H_5)_3\right)_2$, X = C, Si, Ge, Sn [g]

$CrO(O_2)_2(py)$ [h]

$CrO(O_2)_2(bpy)$ [i]

High valent iron complexes:

$[Fe(o\text{-}C_6H_4AsMe_2)_2]^{+2}$ [j]

$[Fe(o\text{-}C_6H_4PMe_2)_2]^{+2}$ [k]

$[Fe(S_2NCR_2)_3]^{+1}$ [l]

$[Fe(TPP)Cl]^{+1}$ [m]

High valent osmium complexes:

$\{OsO_2(O_2R)\}_2$ [n]

$OsO_2(O_2R)(py)_2$ [n]

$OsO(O_2R)_2$ [n]

$OsO_x(NR)_{4-x}$, x = 1, 2, 3 [o]

[a] Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N.J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.*, **1972**, 533; Mowat, W.; Shortland, A.J.; Hill, N.J.; Wilkinson, G. *Ibid.*, **1973**, 770; Kruse, W. *J. Organomet. Chem.*, **1972**, *42*, C39.

[b] Alyea, E.C.; Basi, J.S.; Bradley, D.C.; Chisholm, M.H. *J. Chem. Soc, Sect. A*, **1971**, 772; Dyrkacz, G.; Roček, J. *J. Amer. Chem. Soc.*, **1973**, *95*, 4756; Bochmann, M.; Wilkinson, G.; Young, G.B.; Hursthouse, M.B.; Abdul Malik, K.M. *J. Chem. Soc., Dalton Trans.*, **1980**, 1863.

[c] Basi, J.S.; Bradley, D.C.; Chisholm, M.H. *J. Chem. Soc., Sect. A*, **1971**, 1434.

[d] Krumpolc, M.; Roček, J. *Inorg. Syn.*, **1980**, *20*, 63, and references therein.

[e] Sharpless, K.B.; Akashi, K. *J. Amer. Chem. Soc.*, **1975**, *97*, 5927.

[f] Treibs, W.; Schmidt, H. *Chem. Ber.*, **1928**, *61*, 459.

[g] Lyčka, A.; Šnobl, D.; Handlíř, K.; Holeček, J.; Nádvorník, M. *Collect. Czech. Chem. Commun.*, **1981**, *46*, 1383, and references therein.

[h] Stromberg, R. *Arkiv. för Kemi*, **1964**, *22*, 29.

[i] Stromberg, R.; Ainalem, I. *Acta Chemica Scandinavia*, **1968**, *22*, 1439.

[j] Hazeldean, G.S.F.; Nyholm, R.S.; Parish, R.V. *J. Chem. Soc., Sect. A*, **1966**, 162.

[k] Warren, L.F., Bennett, M.A. *Inorg. Chem.*, **1976**, *15*, 3126.

[l] Pasek, E.A.; Straub, D.K. *Ibid.*, **1972**, *11*, 259.

[m] Felton, R.H.; Owens, G.S.; Dolphin, D.; Forman, A.; Borg, D.C.; Fajar, J. *Ann. N.Y. Acad. Sci.*, **1973**, *206*, 504.

[n] Schröder, M. *Chem. Rev.*, **1980**, *80*, 187, and references therein.

[o] Chong, A.O.; Oshima, K.; Sharpless, K.B. *J. Amer. Chem. Soc.*, **1977**, *99*, 3420, and references therein.

Results and Discussion

Synthesis

The chelating ligands used in this study were all synthesized in moderate to high yield from the appropriate diamine and the appropriate 2-acetylsalicylic acid (Scheme 1.2). The acids were cleanly converted to the corresponding acid chlorides using oxalyl chloride and readily formed amides on mixing with dichloromethane solutions of the diamine. Treatment of the residues with aqueous base facilitated cleavage of the acetyl groups; reacidification precipitated the desired compounds from the aqueous solution. White microcrystalline solids were recovered on recrystallization, typically from acetone/water. The complex, 1,2-bis(2-hydroxybenzamido)ethane, was easily converted to the tetrachlorinated derivative, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane, using chlorine gas with glacial acetic acid as the solvent. This compound cocrystallized with pyridinium chloride and has been structurally characterized by *X*-ray crystallography. The structure has provided a benchmark for discussion of the structural parameters of the transition metal complexes of H_4CHBA-Et and related ligands. (See Results and Discussion, *X*-ray Crystallography.)

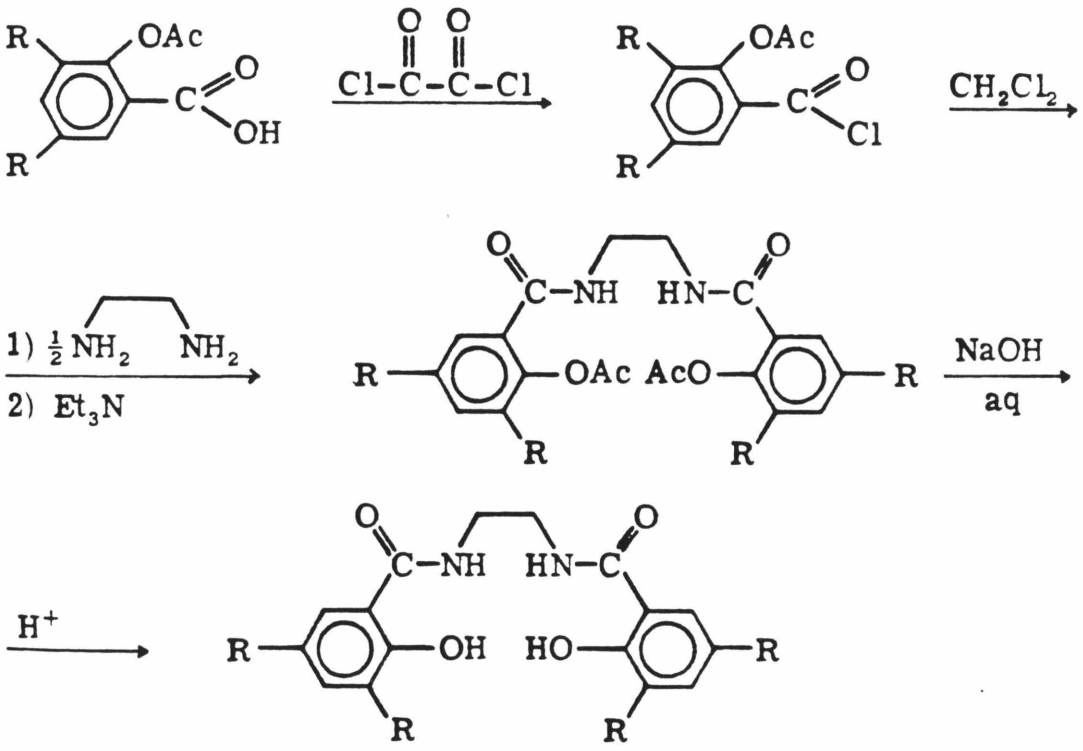
Attempts to complex these potential ligands to chromium were made via both high valent species, *e.g.*, CrO_3, CrO_2Cl_2, $Na[CrO(OC(O)C(CH_3)_2O)_2]$, and $Cr(O\text{-}t\text{-}Bu)_4$, and chromium(III) compounds: $CrCl_3 \cdot 3thf$ and $CrCl_3 \cdot 6H_2O$. Only with $CrCl_3 \cdot 6H_2O$ were tractable complexes isolable. Coordination compounds were made with the following chelates: 1,2-bis(2-hydroxybenzamido)ethane, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane, and 1,2-bis(2-hydroxybenzamido)-benzene.[†]

From a solution of $CrCl_3 \cdot 6H_2O$ (1 equiv.) and the bis-hydroxybenzamido ligand (1 equiv.), which had been refluxed over anhydrous sodium carbonate, two types of coordination complexes were obtained. Microcrystalline green powders (Type I) were collected on immediate addition of a suitable precipitating agent

---

[†] Abbreviated $(H)_4$HBA-Et, $(H)_4$CHBA-Et, and $(H)_4$HBA-*o*Bz, respectively.

Scheme 1.2. Synthetic route to the bis-hydroxybenzamido ligands used here.


R
OAc
C
O
OH
R
Cl–C–C–Cl
O O
R
OAc
C
O
Cl
R
CH2Cl2
1) ½ NH2 NH2
2) Et3N
C–NH HN–C
O O
R
OAc AcO
R
R R
NaOH
aq
H+
C–NH HN–C
O O
R
OH HO
R
R R

and, in one instance, a dimeric crystalline complex (Type II) was obtained from a pyridine solution after several weeks.

Infrared spectra of the Type I compounds‡ have pronounced bands in the 3200–3600 cm^{-1} region suggesting the presence of hydrated/coordinated water or hydroxyl groups. Infrared bands attributed to the ligand carbonyl stretching modes shifted to lower energy by 28–40 cm^{-1}. Using resonance arguments, both *N*-bound and *O*-bound complexes are consistent with this observation (Scheme 1.3). The elemental analyses were also in agreement with two formulations — one with *N*-bound organic amide groups, chelating to one metal, the other with *O*-bound amide groups, forming a dimeric or polymeric complex — as shown in Figure 1.7a,b. In both cases they are sodium salts.

Direct evidence for either assignment has not been forthcoming. Cation exchange has not been successful and attempts to measure the conductivity and the molecular weight have been hindered by poor solubility in suitable solvents. Attempts to oxidize these complexes by various chemical means,* with hopes of obtaining characterizable species with chromium in a higher valency, have also been unsuccessful. Indirect arguments for the dimeric/polymeric structure can be made if the Type II compound is considered.

This second coordination mode was discovered when an *X*-ray crystallographic study was undertaken on crystals which had deposited from a pyridine solution after several weeks. As shown in Figure 1.7c, the ligand was found to bridge the two chromium centers forming an unusual dimeric complex, coordinating via the two deprotonated phenolic oxygen atoms, a deprotonated amide nitrogen atom, and an amide-carbonyl oxygen atom. (See Results and Discussion, *X*-ray Crystallography.) Since the Type I complexes precede the formation of neutral dimers, such as $\{Cr((H)(CHBA\text{-}Et))(py)_2\}_2$, *i.e.*, immediate precip-

‡ Although the characterized complexes were synthesized in other solvents, Type I materials from pyridine exhibited identical infrared spectra.

* Oxidants tried were: hydrogen peroxide, *m*-chloroperbenzoic acid, *meta*-sodium periodate, iodosylbenzene, and *t*-butyl hydroperoxide.

Scheme 1.3. Resonance structures for *N*- and *O*-complexed organic amide groups.

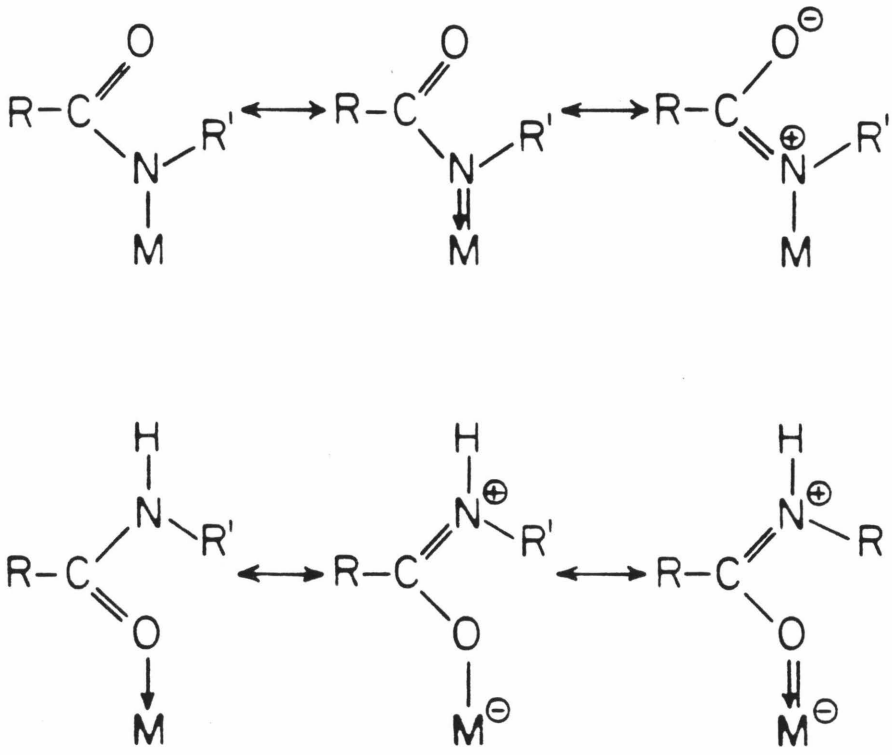
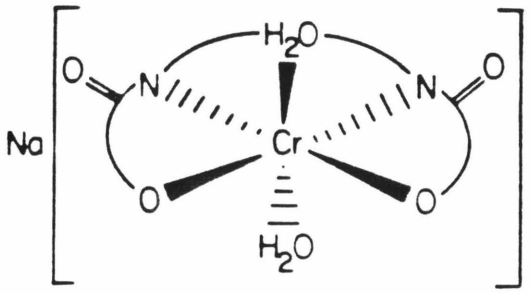
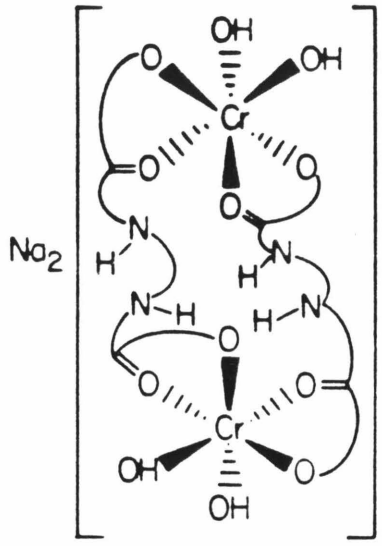


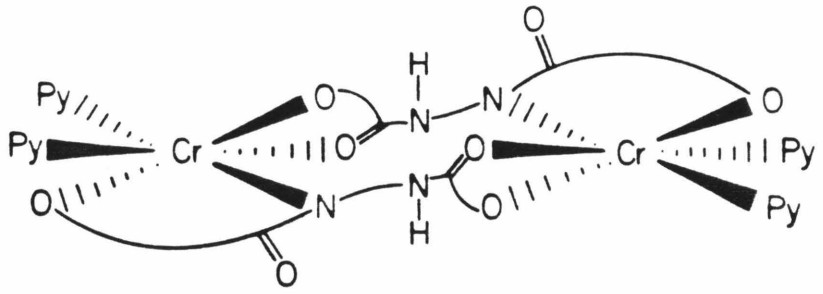
Figure 1.7. Possible formulations for the Type I compounds and schematic structure of the Type II chromium dimer.


Na
O
N
H2O
Cr
O
N
O
O
H2O

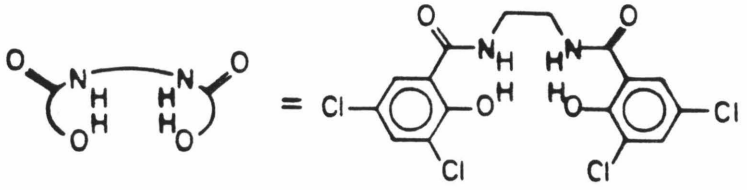
a


Na2
OH
O
Cr
OH
O
O
N
H
N
H
N
H
N
H
O
O
O
Cr
O
OH
OH

b


Py
Py
Cr
O
O
H
N
N
O
O
O
Cr
Py
Py
O
N
N
H
O
O

c


O
N
H
N
H
O
=
O
N
H
N
H
O
Cl
OH
OH
Cl
Cl
Cl

itation rather than extended exposure to pyridine, it is likely that these Type I salts are also dimeric or polymeric (Figure 1.7b). Had the *N*-bound complex (Figure 1.7a) formed first, it is unlikely that it would react with the solvent, pyridine, to dissociate the phenoxide, which would be necessary to form the observed Type II dimer. The Type I dimeric/polymeric structure is reasonable, if the possible acid-base equilibria are considered. Under basic conditions, three fundamental reactions can occur: i) metal hydrolysis (equation 4), ii) phenoxide coordination (equation 5), and iii) chelate-assisted *N*-coordination of the organic amide (equation 6).

$$[\mathrm{M\text{–}OH_2}]^{n+} \rightleftharpoons [\mathrm{M\text{–}OH}]^{(n-1)+} + \mathrm{H^+} \quad (4)$$

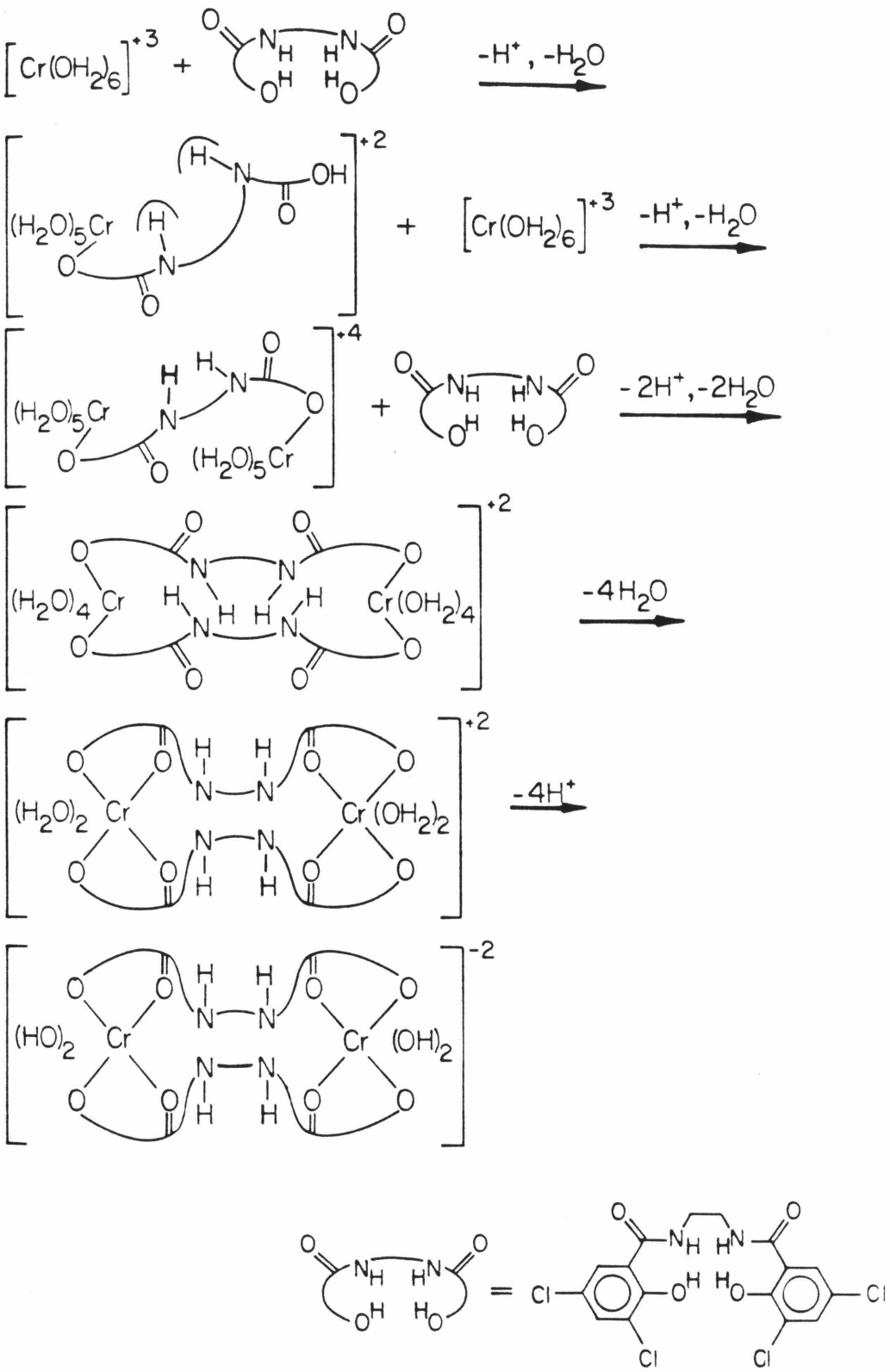
$$\mathrm{M}^{n+} + \mathrm{ArOH} \rightleftharpoons [\mathrm{M\text{–}OAr}]^{(n-1)+} + \mathrm{H^+} \quad (5)$$

$$\mathrm{M}^{n+} + \mathrm{R'CONRH} \rightleftharpoons [\mathrm{M\text{–}NRCOR'}]^{(n-1)+} + \mathrm{H^+} \quad (6)$$

As shown in Scheme 1.4, the first chelation step is most likely coordination of a phenol ($pK_a \approx 7$–8[29]). Then two plausible reactions could occur: i) the deprotonation and coordination of the second phenol or ii) the chelate assisted *N*-coordination of the organic amide group. Even in organic solvents it is doubtful that the equilibrium of the latter reaction could be shifted substantially to compete with phenol deprotonation and coordination in this system. This reaction has not been shown to compete effectively with metal hydrolysis which occurs at $pK_a = 9.4$ in aqueous solution;[30] *cf.* the reactivity of amide groups with Os(VI), Cu(II), Ni(II), and Co(II). Therefore, the next step would be attack by the phenol situated at the other end of the ligand. Coordination to the same chromium ion is not possible due to the geometric constraints and steric demands of the amide groups; thus monomers are disfavored when the amide nitrogen atoms will not readily deprotonate and coordinate to the metal.

Analogous dimeric/polymeric complexes have been postulated. Titrations of cupric ion and *N,N'*-diglycyl-1,2-ethanediamine (H_2L) with sodium hydroxide were found to be very complex. A satisfactory model for the complexation process, derived from the simultaneous spectrophotometric and potentiometric data,

Scheme 1.4. Proposed coordination pathway for bis-hydroxybenzamido ligands to chromium(III).

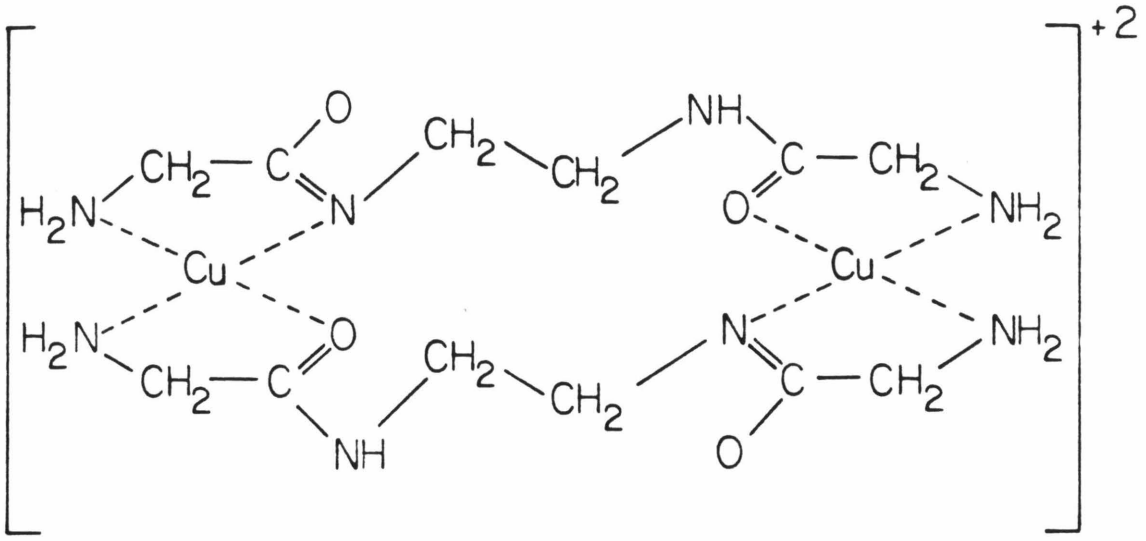


includes two dimeric species, $[Cu_2(HL)_2]^{+2}$ and $[Cu_2(H_2L)_2]^{+4}$ (Figure 1.8).[31] Vagg, *et al.*, have investigated the reactivity of several transition metal salts with derivatives of 1,2-bis(2-pyridinecarboxamido)ethane (H_2L'). Thermogravimetric analysis of complexes with non-deprotonated ligands (*e.g.*, $Mn(H_2L')Cl_2$, $Fe(H_2L')Cl_2$, or $Co(H_2L')Cl_2$) exhibited a decomposition pattern suggestive of a polymeric material; these compounds were also found to be fairly insoluble. A proposed coordination mode is shown in Figure 1.9.[32]

If the Type I and Type II complexes have the chelating ligands coordinated in nearly the same way, similar infrared spectra might also be expected. Interestingly, the infrared spectra of the Type II complex were found to be significantly different than the corresponding spectra of the Type I material. The crystalline neutral dimer exhibits a strong band at 1508 cm^{-1} which has been tentatively assigned to the ν(CO) for the *O*-coordinated amido carbonyl. The Type I salt, on the other hand, has no infrared bands in this region, but does have strong bands from 1570–1610 cm^{-1}. The ν(NH) in the neutral dimer appears as a weak broad band centered near 3200 cm^{-1}; all of the Type I complexes have a strong broad band extending from 3200–3600 cm^{-1}, which has a profile typical of hydrated/coordinated water or hydroxyl groups. To probe this situation further, the coordination complex of $CrCl_3 \cdot 3H_2O$ and 1,2-bis(*N*-methyl-2-hydroxybenzamido)ethane ($(H)_2$*N*HMBA-Et) was synthesized. Here the ligand cannot coordinate through the amide nitrogen, since it is blocked by the methyl group, thus preventing the formation of monomers. Although this complex was not obtained analytically pure (possibly due to chromic hydroxide contamination), the infrared spectra of the crude material was nearly identical to that of the Type I $CrCl_3 \cdot 3H_2O/(H)_4$HBA-Et complex. This result suggests the two complexes are very similar or that infrared spectroscopy is not a useful means of characterization for these complexes.

The coordination chemistry of iron(III) with these ligands was found to be analogous to the chemistry described above; the infrared spectra were identical

Figure 1.8. Dimeric species thought to form when cupric ion and *N*,*N*′-diglycl-1,2-ethanediamine was titrated with aqueous sodium hydroxide.


+2
O
CH2
C
N
CH2
CH2
NH
C
CH2
H2N
O
NH2
Cu
Cu
H2N
O
N
NH2
CH2
C
CH2
CH2
C
CH2
NH
O

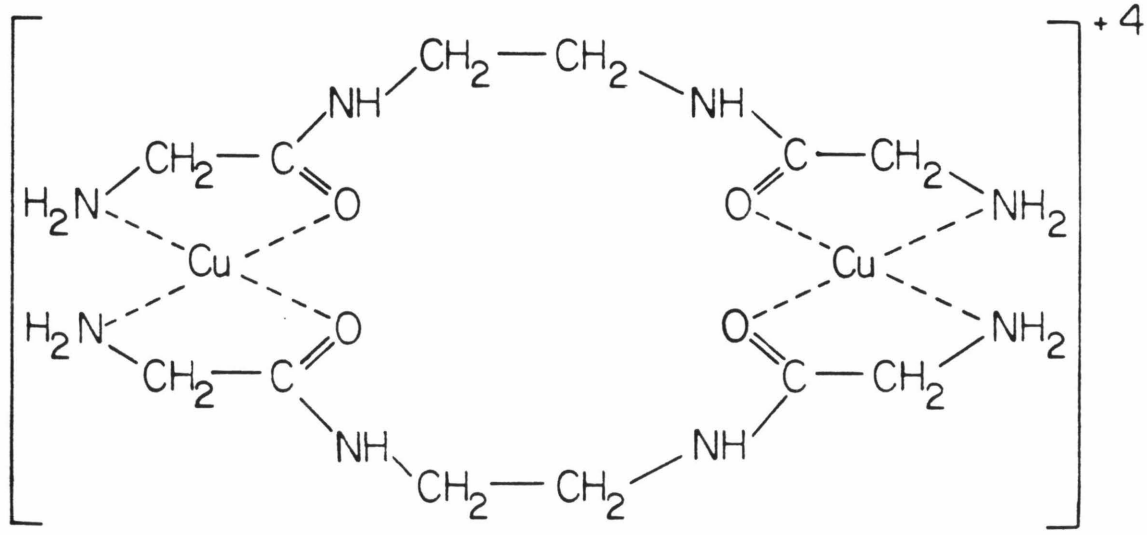
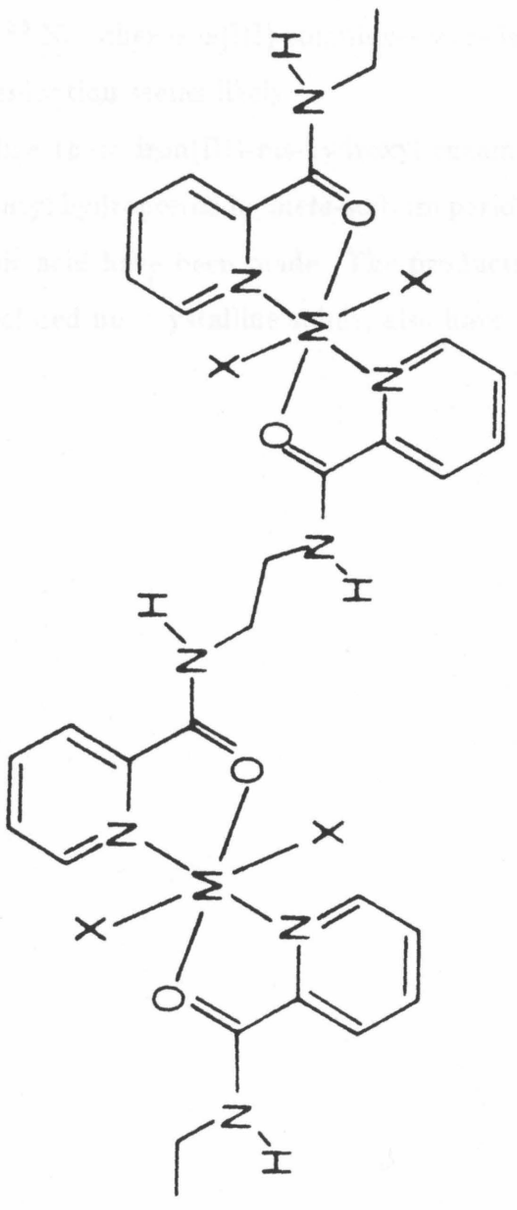

+4
CH2
CH2
NH
NH
CH2
C
C
CH2
H2N
O
O
NH2
Cu
Cu
H2N
O
O
NH2
CH2
C
C
CH2
NH
NH
CH2
CH2

Figure 1.9. Proposed coordination modes of bis-pyridinecarboxamido ligands with Mn^{+2}, Fe^{+2}, Co^{+2}.



to the corresponding Type I chromium(III) compounds. It is likely that coordination of the bis-hydroxybenzamido ligands is also the same. The complex with $(H)_4$HBA-Et has been characterized by infrared spectroscopy, elemental analysis, and magnetic susceptibility measurements. The magnetic moment was found to be significantly lower than the theoretical value for high-spin d^5 system. It is possible that this molecule exhibits intermediate spin as was found for an iron(III) prophyrinato complex.[33] No other iron(III) complexes were isolated in pure form; ferric hydroxide contamination seems likely.

Attempts to oxidize these iron(III)-bis-hydroxybenzamido complexes with hydrogen peroxide, *t*-butyl hydroperoxide, *meta*-sodium periodate, iodosylbenzene, and *m*-chloroperbenzoic acid have been made. The products of these reactions, dark brown or black colored noncrystalline solids, also have not been isolated in pure form.

X-ray Crystallography

X-ray Crystallography has played a major role in the characterization of the transition metal complexes involving these bis-hydroxybenzamido ligands. It has been especially useful when the nuclear magnetic resonance spectroscopic data were ambiguous or nonexistent. Five structure determinations are reported here, including the free ligand, $(H)_4$CHBA-Et. Refined atomic coordinates and Gaussian thermal parameters appear in the Experimental section; structure factor tables for compounds which have not been reported in the literature appear in Appendices A–C.

$(H)_4$CHBA-Et·pyHCl.

We have been fortunate to obtain crystals of this ligand which was found to cocrystallize with pyridinium chloride. It has proved to be a useful benchmark for comparisons of structural data of many bis-hydroxybenzamido complexes. A comparative listing appears in Table 1.9 below.

As with other salicylic derivatives the phenolic oxygen atoms were found to be coplanar with the carbonyl group (Figure 1.10).[34] Hydrogen bonding between the phenol hydrogen atoms† and the amide carbonyl oxygen atoms was also observed. The H···O contacts (1.659(3) and 1.741(3)Å) are similar to those found in salicylic acid (1.704Å).[35]

The chloride ion was found to be near the pyridinium ion (Cl^-–H_{PN} 2.009(1)Å) and also in close proximity to the amide hydrogen atoms‡ on the ligand framework (Cl^-–H_{N1} 2.611(1) and Cl^-–H_{N2} 2.267(1)Å). The hydrogen bonding to the chloride ion may be responsible for the observed *gauche* conformation about the ethylene bridge in the molecule; considering steric factors, the *anti* conformation should be more stable. Packing forces may also play a major role. Bond lengths and bond angles are given in Table 1.3 and Table 1.4.

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† Located on a difference Fourier map.

‡ In idealized positions.

Figure 1.10. ORTEP view of $(H)_4$CHBA-Et·pyHCl.

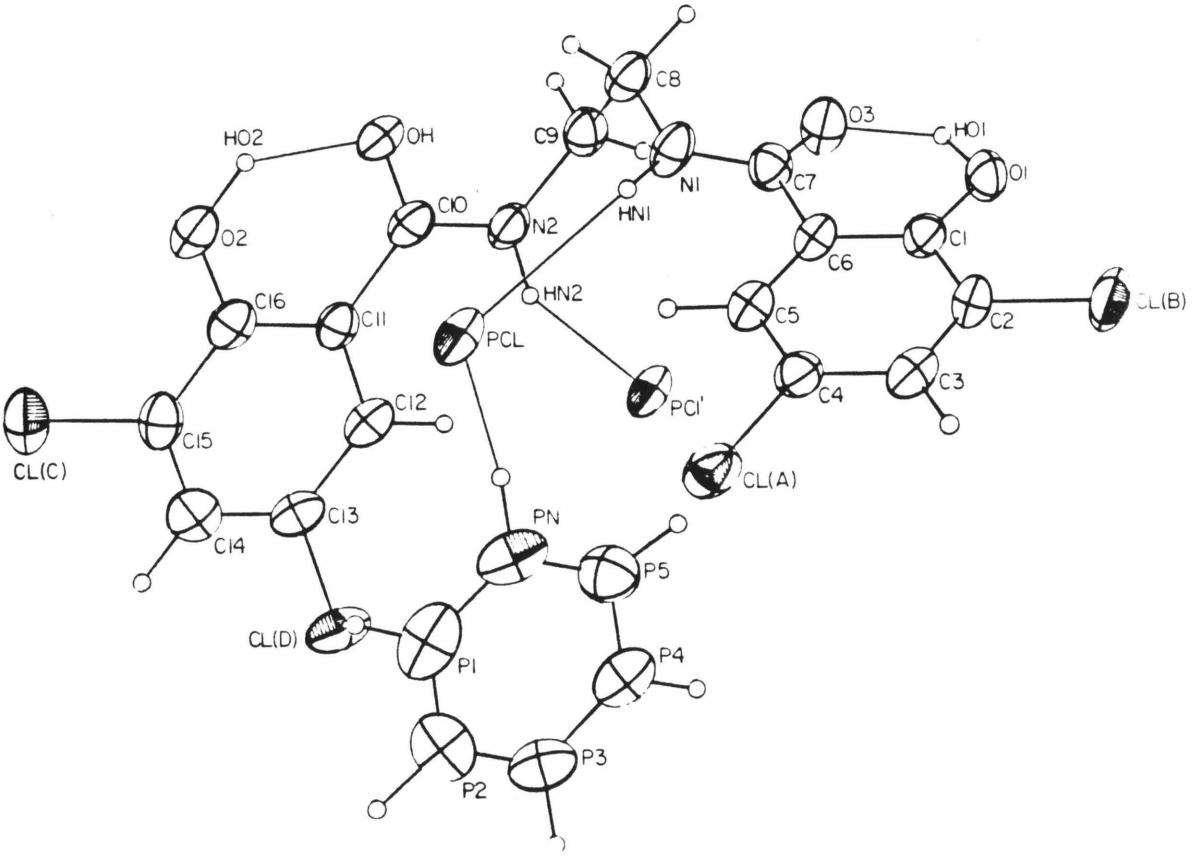

C8
C9
O3
HO1
HO2
OH
N1
C7
O1
C10
N2
HN1
O2
C1
C6
HN2
C16
C11
C5
C2
CL(B)
PCL
PCl'
C4
C3
C12
C15
CL(C)
CL(A)
C13
PN
C14
P5
CL(D)
P1
P4
P3
P2

Table 1.3. Bond lengths (in angstroms) for the molecular structure of $(H)_4$CHBA-Et·pyHCl.

CLA-C4	1.749(5)
CLB-C2	1.742(5)
CLC-C15	1.737(5)
CLD-C18	1.749(5)
O1-C1	1.351(5)
O1-HO1	0.986(9)
O2-C16	1.352(5)
O2-HO2	1.000(9)
O3-C7	1.247(5)
O4-C10	1.244(6)
N1-C7	1.334(6)
N1-C8	1.467(6)
N2-C9	1.460(6)
N2-C10	1.323(6)
C1-C2	1.414(6)
C1-C6	1.401(6)
C2-C3	1.360(6)
C3-C4	1.385(6)
C4-C5	1.378(6)
C5-C6	1.388(6)
C6-C7	1.501(6)
C8-C9	1.536(6)
C10-C11	1.486(6)
C11-C12	1.409(6)
C11-C16	1.400(6)
C12-C13	1.379(6)
C13-C14	1.369(7)
C14-C15	1.378(6)
C15-C16	1.393(6)
PN-P1	1.324(7)
PN-P5	1.328(7)
P1-P2	1.360(8)
P2-P3	1.380(8)
P3-P4	1.355(8)
P4-P5	1.359(8)

Table 1.4. Bond angles (in degrees) for the molecular structure of $(H)_4$CHBA-Et·pyHCl.

C1-O1-HO1	107.9(9)	N2-C10-O4	121.2(4)
C16-O2-HO2	117.9(9)	N2-C10-C11	116.7(4)
C7-N1-C8	121.4(4)	O4-C10-C11	120.0(4)
C9-N2-C10	123.0(4)	C10-C11-C12	121.9(4)
O1-C1-C2	119.3(4)	C10-C11-C16	118.8(4)
O1-C1-C6	123.3(4)	C12-C11-C16	119.2(4)
C2-C1-C6	117.4(4)	C11-C12-C13	119.4(4)
CLB-C2-C1	118.3(3)	CLD-C13-C12	118.8(4)
CLB-C2-C3	118.8(4)	CLD-C13-C14	119.1(4)
C1-C2-C3	122.9(4)	C12-C13-C14	122.0(4)
C2-C3-C4	117.8(4)	C13-C14-C15	118.5(4)
CLA-C4-C3	118.3(3)	CLC-C15-C14	118.7(4)
CLA-C4-C5	119.6(3)	CLC-C15-C16	119.2(3)
C3-C4-C5	122.1(4)	C14-C15-C16	121.9(4)
C4-C5-C6	119.6(4)	O2-C16-C11	118.8(4)
C1-C6-C5	120.2(4)	O2-C16-C15	119.1(4)
C1-C6-C7	117.3(4)	C11-C16-C15	122.1(4)
C5-C6-C7	122.5(4)	P1-PN-P5	122.1(5)
O3-C7-N1	122.2(4)	PN-P1-P2	119.4(5)
O3-C7-C6	120.7(4)	P1-P2-P3	119.7(5)
N1-C7-C6	117.1(4)	P2-P3-P4	119.1(5)
N1-C8-C9	113.5(4)	P3-P4-P5	119.6(5)
C8-C9-N2	113.2(4)	P4-P5-PN	120.0(5)

$\{Cr((H)CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$.

This was one of the first bis-hydroxybenzamido complexes examined by our group. It has alerted us to the fact that several coordination modes are available to these ligands. This is also the first structurally characterized example of *N*-bound organic amide coordination to chromium(III). Very few complexes of this type are known for the earlier transition metals.[36] The ambidentate nature of the organic amide functional group is also evident, showing that both forms of monodentate amide coordination are possible, at least where the amide is part of a larger chelating system. We have compared the metric data for these two groups below.

The structure consists of discrete dimers and disordered solvent molecules of pyridine. An ORTEP view (Figure 1.11) gives the metrical details on the immediate ligation about the chromium centers. The distorted octahedral environment includes the pyridine nitrogen atoms, an amide nitrogen atom, the phenolic oxygen atoms, and an amide carbonyl oxygen atom; the coordinated pyridine ligands are *cis* and the phenolic oxygen atoms are *trans*. Complete listings of bond lengths and bond angles are given in Table 1.5 and Table 1.6.

The $Cr\text{–}N_{amide}$ bond length is 2.030(6)Å and the two $Cr\text{–}N_{phenol}$ bond lengths are 1.915(5) and 1.931(5)Å; similar metal–ligand contacts are found for $[Cr(salen)(H_2O)_2]Cl$: Cr–N 2.005(9) and 1.997(8)Å, Cr–O 1.916(8) and 1.952(8)Å.[37] The $Cr\text{–}O_{carbonyl}$ bond length is 1.976(5)Å, which is somewhat longer than the 1.91(2)Å $Cr\text{–}O_{carbonyl}$ bond length found in *mer*-trichloro-(*N,N'*-dimethylformamide)(1,10-phenanthroline)chromium(III).[38]

For the first time a direct comparison between both forms of monodentate organic amide coordination has been possible; both amide groups were found *trans* to pyridine. The $Cr\text{–}N_{pyridine}$ bond lengths (2.145(6)Å, *trans*-to-N and 2.097(6)Å, *trans*-to-O) indicate a greater *trans* influence for the *N*-coordinated *vs.* the *O*-coordinated amido ligand. Interestingly, the $C_{carbonyl}\text{–}N_{amide}$ bond length for the *N*-coordinated amide is longer than that found in the free ligand: 1.365(9)

Figure 1.11. ORTEP view of $\{Cr((H)CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$. Bond lengths for the coordination sphere of the chromium atoms are in angstroms.

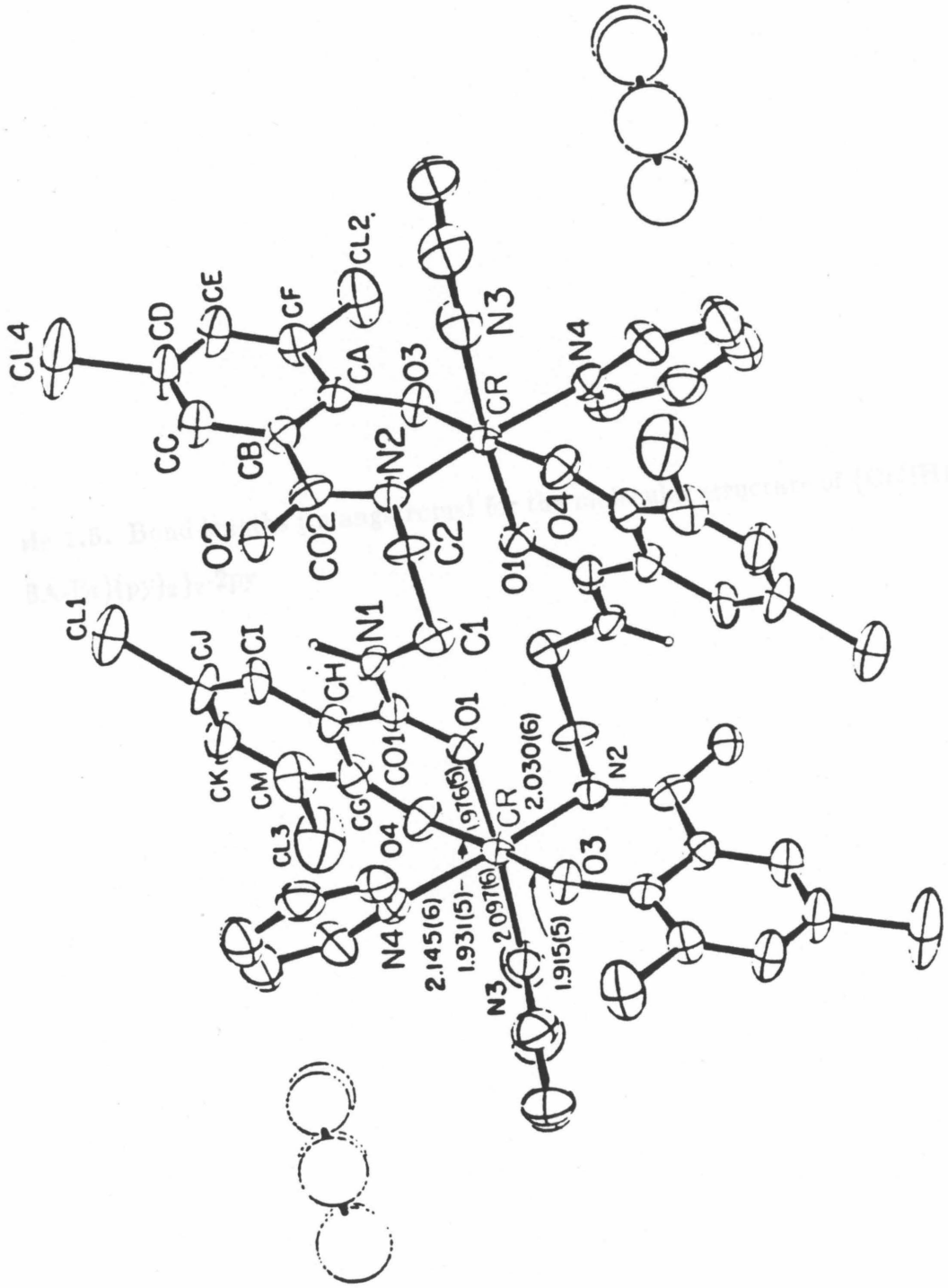

CL4
CD
CE
CF
CL2
CA
O3
CR
N3
N4
CC
CB
N2
O4
O2
CO2
C2
O1
CL1
CJ
CI
N1
C1
CH
CK
CM
CO1
O1
CG
CL3
O4
1.916(6)
CR
2.030(6)
N2
O3
2.145(6)
1.931(5)
2.097(6)
1.915(5)
N4
N3

Table 1.5. Bond lengths (in angstroms) for the molecular structure of $\{Cr((H)\text{-}CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$.

CR-O1	1.976(05)	CK-CM	1.340(12)
CR-O3	1.915(05)	CG-CM	1.424(11)
CR-O4	1.931(05)	CL1-CJ	1.750(08)
CR-N2	2.030(06)	CL2-CF	1.730(08)
CR-N3	2.097(06)	CL3-CM	1.759(08)
CR-N4	2.145(06)	CL4-CD	1.767(09)
N1-C1	1.486(09)	N3-P1	1.327(10)
N1-CO1	1.343(09)	P1-P2	1.402(13)
N2-C2	1.474(09)	P2-P3	1.363(14)
N2-CO2	1.365(09)	P3-P4	1.375(13)
C1-C2	1.560(10)	P4-P5	1.391(12)
CO1-O1	1.278(09)	N3-P5	1.344(10)
O3-CA	1,322(08)	N4-P6	1.340(10)
O4-CG	1.302(09)	P6-P7	1.376(12)
CO1-CH	1.487(10)	P7-P8	1.381(13)
CO2-O2	1.270(09)	P8-P9	1.397(13)
CO2-CB	1.504(10)	P9-P10	1.388(11)
CA-CB	1.427(10)	N4-P10	1.345(10)
CB-CC	1.405(10)		
CC-CD	1.353(11)	Solvent Molecule:	
CD-CE	1.380(11)		
CE-CF	1.360(11)	P11-P12	1.34 (2)
CA-CF	1.417(10)	P12-P13	1.40 (2)
CG-CH	1.435(11)	P13-P14	1.40 (2)
CH-CI	1.408(10)	P14-P15	1.33 (2)
CI-CJ	1.360(11)	P15-P16	1.44 (2)
CJ-CK	1.429(12)	P11-P16	1.32 (2)

Table 1.6. Bond angles (in degrees) for the molecular structure of $\{Cr((H)\text{-}CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$.

O1-CR-O2	91.2(2)	O3-CA-CB	124.7(6)	CG-CM-CK	126.4(8)
O1-CR-O4	88.1(2)	O3-CA-CF	120.1(6)	CR-N3-P1	121.5(5)
O1-CR-N2	91.4(2)	CB-CA-CF	115.0(6)	CR-N3-P5	119.5(5)
O1-CR-N3	175.6(2)	C02-CB-CA	123.3(6)	P1-N2-P5	118.9(7)
O1-CR-N4	86.7(2)	CO2-CB-CC	116.7(6)	N3-P1-P2	122.4(8)
O3-CR-O4	175.8(2)	CA-CB-CC	119.9(7)	P1-P2-P3	118.9(9)
O3-CR-N2	92.8(2)	CA-CC-CD	120.1(7)	P2-P3-P4	118.8(9)
O3-CR-N3	90.4(2)	CL4-CD-CC	118.6(6)	P3-P4-P5	120.0(8)
O3-CR-N4	89.7(2)	CL4-CD-CE	118.3(6)	N3-P5-P4	121.0(8)
O4-CR-N2	91.3(2)	CC-CD-CE	122.9(7)	CR-N4-P6	121.4(5)
O4-CR-N3	90.0(2)	CD-CE-CF	116.8(7)	CR-N4-P10	118.1(5)
O4-CR-N4	86.2(2)	CL2-CF-CA	117.0(5)	N4-P6-P7	124.0(8)
N2-CR-N3	92.5(2)	CL2-CF-CE	117.9(6)	P6-P7-P8	117.8(8)
N2-CR-N4	177.0(2)	CA-CF-CE	125.1(7)	P7-P8-P9	119.0(8)
N3-CR-N4	89.2(2)	O4-CG-CH	126.4(7)	P8-P9-P10	119.5(8)
C1-N1-CO1	122.1(6)	O4-CG-CM	119.1(7)	N4-P10-P9	121.1(7)
CR-N2-C2	120.8(4)	CH-CG-CM	114.4(7)		
CR-N2-CO2	124.8(5)	CO1-CH-CG	118.9(6)	Solvent Molecule:	
C2-N2-CO2	114.1(6)	CO1-CH-CI	120.3(6)		
N1-C1-C2	107.0(6)	CG-CH-CI	120.8(6)	P12-P11-P16	124.2(11)
N2-C2-C1	111.0(6)	CH-CI-CJ	119.9(7)	P11-P12-P13	119.4(12)
N1-CO1-O1	117.9(6)	CL1-CJ-CI	119.2(6)	P12-P13-P14	115.1(13)
N1-CO1-CH	118.6(6)	CL1-CJ-CK	118.6(6)	P13-P14-P15	126.3(14)
O1-CO1-CH	123.5(6)	CI-CJ-CK	122.2(7)	P14-P15-P16	114.8(14)
N2-CO2-O2	122.6(7)	CJ-CK-CM	116.3(8)	P11-P16-P15	199.7(12)
N2-CO2-CB	121.6(6)	CL3-CM-CG	116.1(6)		
O2-CO2-CB	115.8(6)	CL3-CM-CK	117.4(6)		

vs. 1.328(6)Å(ave.). The opposite effect is observed for metal-bound and free peptides ($C_{carbonyl}$–N_{amide} ave.: 1.30Å, *N*-bound; 1.31Å, *O*-bound; 1.325Å, free).[39] Distortions due to the strain in the bridging chelate can not be discounted. The carbonyl C–O bond lengths are equal for both the coordinated and uncoordinated amide carbonyls (1.278(9) *vs.* 1.270(9)Å); the carbonyl C–O bond length in the free ligand is 1.246(6)Å (ave.). Freeman has reported average peptide carbonyl bond lengths for metal-bound and free peptides; the difference between them is small (C–$O_{carbonyl}$ ave.: 1.26Å, *N*-bound; 1.24Å, *O*-bound; 1.24Å, free).[39]

The chromium–chromium distance in the dimer is 8.9Å.

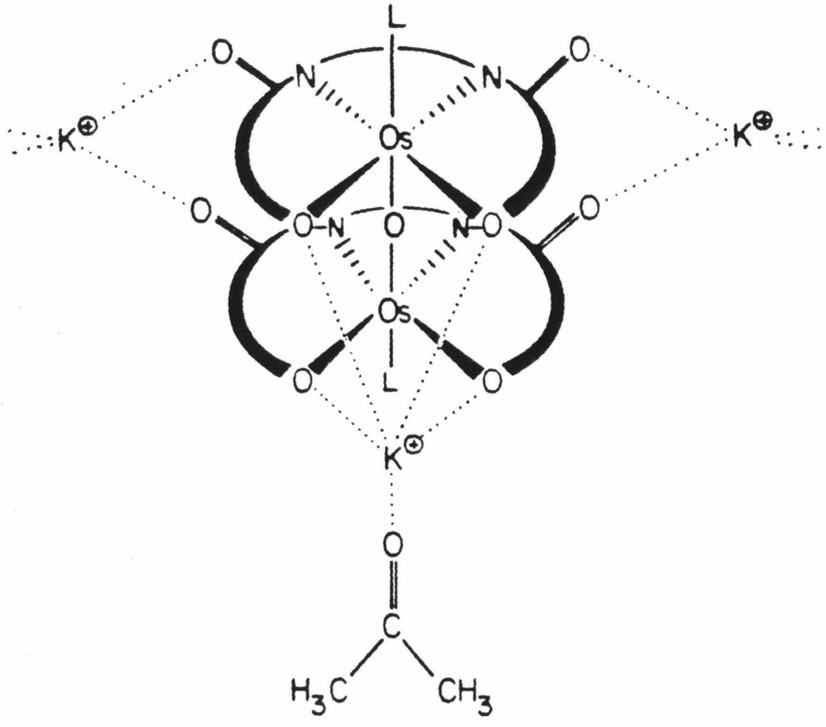
$K_2[\{Os(\eta^4\text{-CHBA-Et})(OPPh_3)\}_2O]\cdot\frac{3}{2}$acetone$\cdot H_2O$.

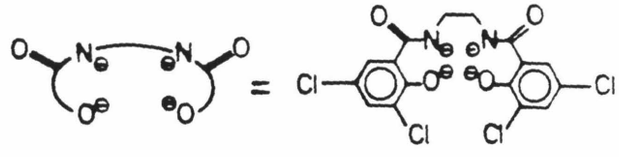
Investigations into the osmium chemistry of these bis-hydroxybenzamido ligands, in collaboration with Dr. J.A. Christie (Audett) and T.E. Krafft, resulted in several crystallographic studies,[18] including this μ-oxo dimer. This structure clearly demonstrated, for the first time, that the bis-hydroxybenzamido ligand could coordinate as a tetradentate tetraanion, via the amide nitrogen atoms and the phenolic oxygen atoms, to one metal center. The structure also exhibited the first examples of bonds between osmium(IV) and an *N*-coordinated organic amide ligand, a phenoxide ligand, and a phosphine oxide ligand.

The bis-hydroxybenzamido ligands in this μ-oxo dimeric complex were found to bind to the osmium(IV) centers in an eclipsed planar fashion (Figure 1.12); the Os–O–Os angle is 175(1)°. The averaged bond lengths and angles in these chelates were found to be very similar to those found in the free ligand: C–O_{phenol} 1.33(2) *vs.* 1.352(2)Å, C–$O_{carbonyl}$ 1.27(2) *vs.* 1.246(6)Å, and C–N_{amide} 1.33(2) *vs.* 1.328(6)Å. Complete metrical data (averaged) appear in Figure 1.13.

This study also revealed unusual coordination environments for the potassium ions. One potassium ion, centered in a square pyramid, is well within binding distance of the four phenolic oxygen atoms (K^+–O_{phenol} 2.87Å ave.) and one acetone solvate molecule (K^+–$O_{acetone}$ 2.80Å) as shown in Figure 1.14; this potassium ion is further coordinated to the μ-oxo ligand (K^+–O_{oxo} 3.16Å).

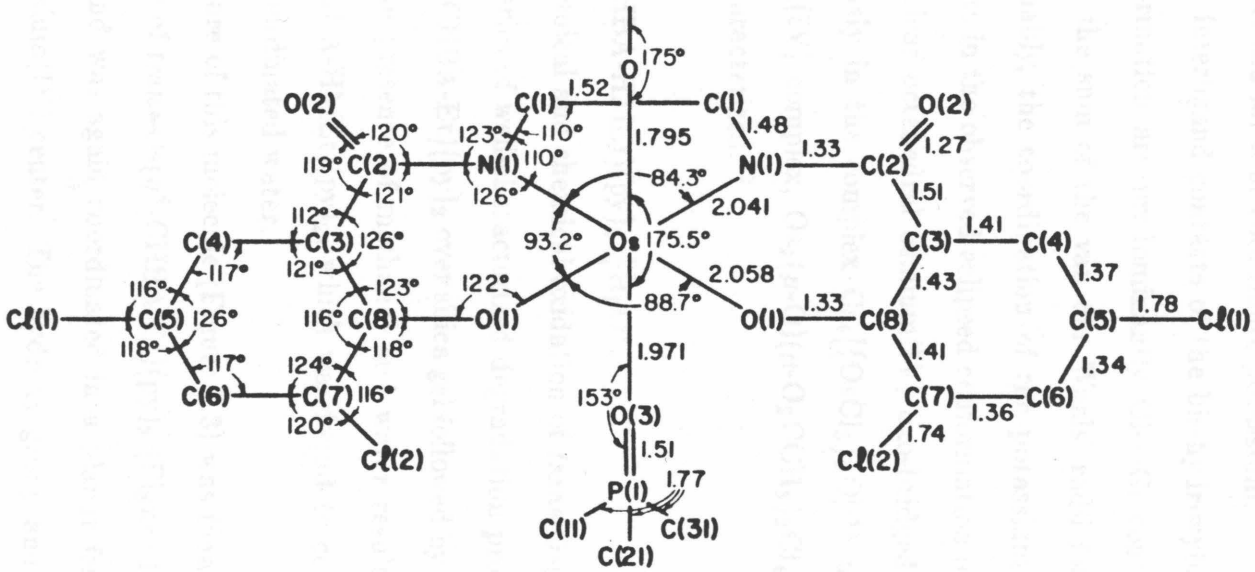
Figure 1.12. Schematic view of $K_2[\{Os(\eta^4\text{-CHBA-Et})(OPPh_3)\}_2O]\cdot\frac{5}{2}$acetone$\cdot H_2O$. The water molecule and the fractional acetone molecule are not shown.





L = $OPPh_3$

Figure 1.13. Structure of $[\{Os(\eta^4\text{-CHBA-Et})(OPPh_3)\}_2O]^{-2}$. Averaged bond lengths (over four sets of atomic positions) are in angstroms and averaged bond angles are in degrees.



Ave. O(3)–P(1)–C ∢ 110°
Ave. C –P(1)–C ∢ 108°

The second potassium ion is apparently four-coordinate, situated at the center of a distorted tetrahedron, linking adjacent anions by bonding with two pairs of eclipsed amide carbonyl oxygen atoms, one pair from each dinuclear unit (K^+–$O_{carbonyl}$ 2.66Å ave.). Low coordination numbers for potassium ions are rare.[40] In fact, this structural study represents the third for five-coordinate potassium and only the second for four-coordinate potassium.

The close interligand contacts of the bis-hydroxybenzamido ligands in this eclipsed conformation are predominantly Cl···Cl contacts, ranging from 3.6–3.9Å, close to the sum of the van der Waals' radii for the two Cl atoms (*ca.* 3.6Å). Presumably, the coordination of the potassium ions plays a significant role, and results in the observed eclipsed conformation of the two planar ligands.

The dinuclear octahedral osmium(IV) oxo-bridged structure has been observed previously in the complex $Cs_4[\{OsCl_5\}_2O]$;[41] a bent oxo bridged dinuclear osmium(IV) complex, $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$, has also been structurally characterized.[42]

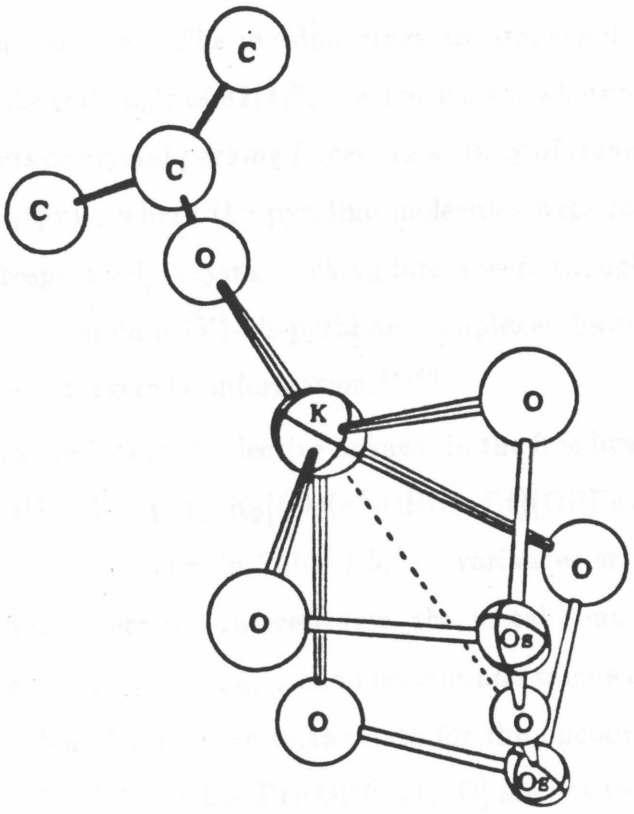
trans-Os(η^4-CHBA-HMEt)(py)$_2\cdot\frac{1}{4}H_2O$*.

Electrochemical and chemical oxidation of *trans*-Os(η^4-CHBA-Et)(py)$_2$ has resulted in a series of well-characterized degradation products. Aerial oxidation of *trans*-Os(η^4-CHBA-Et)(py)$_2$ over silica gel followed by dichlorodicyanoquinone oxidation in the presence of methanol and water resulted in the formation of *trans*-Os(η^4-CHBA-HMEt)(py)$_2$, which was found to cocrystallize with a small amount of uncoordinated water.

The structure of this molecule (Figure 1.3) was found to be nearly identical to the structure of *trans*-Os(η^4-CHBA-Et)(py)$_2$ (Figure 1.4).[18] The bis-hydroxybenzamido ligand was again coordinated in a planar fashion to the equatorial sites of the osmium(IV) center. The hydroxy group and the methoxy group on the five-membered ring (composed of the atoms labeled Os, N1, C8, C9, and N2)

* CHBA-HMEt = the tetraanion of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-1-hydroxy-2-methoxyethane.

Figure 1.14. Potassium ion coordination mode found in the molecular structure of $K_2[\{Os(\eta^4\text{-CHBA-Et})(OPPh_3)\}_2O]\cdot\frac{3}{2}$acetone$\cdot H_2O$.


C
C
C
O
K
O
O
O
Os
O
O
Os

were in the axial positions on C8 and C9, respectively.

The observed *trans* conformation appears to be sterically favored over the *cis* form, where the hydroxy and methoxy groups would be nearly eclipsed. The proposed mechanism for the oxidation steps, discussed elsewhere,[18] requires the formation of the *trans* structure. The bond lengths and bond angles for this structure are given in Table 1.7 and Table 1.8.

Pyridine molecules complete the coordination sphere bonding to the axial positions in the complex. The pyridine rings are staggered with respect to each other with a dihedral angle of 82(4)°; it is not known whether this result is due to electronic effects or crystal packing forces. In a study of *trans*-$Co(acac)_2(py)_2$ and *trans*-$Ni(acac)_2(py)_2$, where the pyridine molecules were found to be staggered and eclipsed, respectively, crystal packing forces were thought to be dominant.[43] Other studies of osmium(IV)-bis-pyridine complexes have found the pyridine molecules in the staggered conformation.[18,44]

A comparative listing of selective linkages in the free ligand $((H)_4$CHBA-Et$)$, *trans*-$Os(\eta^4$-CHBA-Et$)(py)_2$, $K_2[\{Os(\eta^4$-CHBA-Et$)(OPPh_3)\}_2O]$, and *trans*-$Os(\eta^4$-CHBA-HMEt$)(py)_2$ appears in Table 1.9; the variances are small in comparison to the experimental errors. Interestingly, the metal-bound amide groups have somewhat longer $C_{carbonyl}$–N_{amide} bond lengths and somewhat shorter $C_{carbonyl}$–$O_{carbonyl}$ bond lengths, relative to the data for the uncoordinated ligand. (The bond lengths in $K_2[\{Os(CHBA\text{-}Et)(OPPh_3)\}_2O]$ are not very precise.) These results are also directly opposite to the data for coordinated peptide groups noted by Freeman.[39]

trans-$Os(\eta^2$-(H)HBA-TMI$)_2Cl_2\cdot 2DMF$.[§]

The fusion of $(NH_4)_2OsCl_6$ with $(H)_4$HBA-DMBu at temperatures greater than 300°C resulted in the rearrangement of the $(H)_4$HBA-DMBu ligand. Under the severe conditions, one of the amide nitrogen atoms attacked an amide carbonyl carbon atom forming an imidazoline fragment. Presumably, salicylic acid

§ $(H)_2$HBA-TMI = 2-(2′-hydroxyphenyl)-4,4,5,5-tetramethylimidazoline.

Table 1.7. Bond lengths (in angstroms) for the molecular structure of *trans*-Os(CHBA-HMEt)$(py)_2$.

OS-O1	1.973(07)
OS-O2	1.991(07)
OS-N1	1.983(08)
OS-N2	1.976(08)
OS-PN1	2.072(08)
OS-PN2	2.084(08)
CL1-C2	1.722(12)
CL2-C15	1.747(11)
CL3-C4	1.733(14)
CL4-C13	1.742(12)
O1-C1	1.310(12)
O2-C16	1.305(12)
O3-C7	1.264(13)
O4-C10	1.210(15)
O5-C8	1.389(12)
O6-C9	1.422(13)
O6-CME	1.401(17)
N1-C7	1.340(13)
N1-C8	1.477(13)
N2-C9	1.460(13)
N2-C10	1.349(14)
C1-C2	1.393(15)
C1-C6	1.450(14)
C2-C3	1.392(17)
C3-C4	1.358(16)
C4-C5	1.377(18)
C5-C6	1.398(16)
C6-C7	1.484(14)
C8-C9	1.536(14)
C10-C11	1.502(15)
C11-C12	1.409(16)
C11-C16	1.443(15)
C12-C13	1.344(17)
C13-C14	1.366(17)
C14-C15	1.377(16)
C15-C16	1.394(15)
PN1-P1	1.323(14)
PN1-P5	1.333(14)
P1-P2	1.346(18)
P2-P3	1.392(19)
P3-P4	1.343(18)
P4-P5	1.383(17)
PN2-P6	1.340(14)
PN2-P10	1.363(14)
P6-P7	1.367(18)
P7-P8	1.395(19)
P8-P9	1.340(20)
P9-P10	1.310(19)

Table 1.8. Bond angles (in degrees) for the molecular structure of *trans*-Os(CHBA-HMEt)$(py)_2$.

O2-OS-O1	93.1(03)	C6-C7-N1	120.4(09)
N1-OS-O1	92.3(03)	N1-C8-O5	1.9.5(08)
N2-OS-O1	173.6(03)	C9-C8-05	111.3(08)
PN1-OS-O1	92.5(03)	C9-C8-N1	107.9(08)
PN2-OS-O1	84.9(03)	N2-C9-O6	112.2(08)
N1-OS-O2	174.3(03)	C8-C9-O6	106.3(08)
N2-OS-O2	91.6(03)	C8-C9-N2	108.9(08)
PN1-OS-O2	86.3(3)	N2-C10-O4	123.1(10)
PN2-OS-O2	83.4(03)	C11-C11-O4	118.2(10)
N2-OS-N1	83.1(03)	C11-C10-N2	118.7(09)
PN1-OS-N1	89.7(03)	C12-C11-C10	116.4(10)
PN2-OS-N1	96.8(03)	C16-C11-C10	125.2(09)
PN1-OS-N2	92.0(03)	C16-C11-C12	118.3(09)
PN2-OS-N2	92.1(03)	C13-C12-C11	121.7(11)
PN2-OS-PN1	173.1(03)	C12-C13-CL4	120.0(09)
C1-O1-OS	126.9(06)	C14-C13-CL4	118.3(09)
C16-O2-OS	122.9(06)	C14-C13-C12	121.6(11)
CME-O6-C9	114.2(09)	C15-C14-C13	118.4(11)
C7-N1-OS	129.2(07)	C14-C15-CL2	118.8(09)
C8-N1-OS	114.3(06)	C16-C15-CL2	117.4(08)
C8-N1-C7	116.5(08)	C16-C15-C14	123.7(10)
C9-N2-OS	112.5(06)	C11-C16-O2	124.7(09)
C10-N2-OS	128.0(07)	C15-C16-O2	119.0(09)
C10-N2-C9	119.5(08)	C15-C16-C11	116.2(09)
C2-C1-O1	118.3(09)	P1-PN1-OS	121.1(07)
C6-C1-O1	125.3(09)	P5-PN1-OS	125.2(07)
C6-C1-C2	116.4(09)	P5-PN1-P1	113.6(09)
C1-C2-CL1	118.2(08)	P2-P1-PN1	125.3(11)
C3-C3-CL1	118.8(09)	P3-P2-P1	119.6(12)
C3-C2-C1	122.9(11)	P4-P3-P2	117.2(12)
C4-C3-C2	119.0(12)	P5-P4-P4	118.5(12)
C3-C4-CL3	118.9(10)	P4-P5-PN1	125.7(11)
C5-C4-CL3	119.6(10)	P6-PN2-OS	125.8(07)
C5-C4-C3	121.4(12)	P10-PN2-OS	119.3(07)
C6-C5-C4	120.7(11)	P10-PN2-P6	114.8(09)
C5-C6-C1	119.1(09)	P7-P6-PN2	122.3(11)
C7-C6-C1	124.8(09)	P8-P7-P6	120.2(12)
C7-C6-C5	115.9(09)	P9-P8-P7	116.6(13)
N1-C7-O3	122.4(09)	P10-P9-P8	121.0(13)
C6-C7-O3	117.2(09)	P9-P10-PN2	125.1(12)

Table 1.9. A comparative listing of selective linkages in the free ligand (η^4-$(H)_4$CHBA-Et), *trans*-Os(η^4-CHBA-Et)$(py)_2$, $K_2[\{Os(\eta^4\text{-CHBA-Et})(OPPh_3)\}_2O]$, and *trans*-Os($\eta^4$-CHBA-HMEt)$(py)_2$ (in angstroms).

	A	B[a]	C	D
$Os–N_{amide}$	—	1.969(4)	2.024(26)	1.980(1)
$Os–O_{phenol}$	—	1.999(3)	2.038(19)	1.984(1)
$C–O_{phenol}$	1.352(5)	1.331(5)	1.341(40)	1.307(1)
$C–O_{carbonyl}$	1.245(6)	1.228(6)	1.267(43)	1.237(1)
$C_{carbonyl}–N_{amide}$	1.328(6)	1.355(6)	1.340(44)	1.344(1)

A = $(H)_4$CHBA-Et

B = *trans*-Os(CHBA-Et)$(py)_2$

C = $K_2[\{Os(CHBA\text{-}Et)(OPPh_3)\}_2O]$

D = *trans*-Os(CHBA-HMEt)$(py)_2$

[a] Anson, F.C.; Christie, J.A.; Collins, T.J.; Coots, R.J.; Furutani, T.T.; Gipson, S.L.; Keech, J.T.; Krafft, T.E.; Santarsiero, B.D.; Spies, G.H. *J. Amer. Chem. Soc.*, **1984**, *106*, 4460.

was extruded. The role of the osmium(VI) ion in this process is not known.

Crystals were obtained from a DMF solution of the extracted residues. This unusual structure consists of discrete monomers bearing axial chloride ligands and two bidentate monoanionic phenoxy-imidazoline ligands in the equatorial positions disposed mutually *trans* (Figure 1.15). Solvated DMF molecules were also found.

This is the first reported structure determination of an osmium(IV)-imidazoline complex, though complexes of the 2-*o*-phenoxyimidazole ligand are known.[45] The Os–O bond length (1.995(12)Å) was found to be similar to those found in the osmium(IV)-bis-hydroxybenzamido complexes described above. The Os–$N_{imidazoline}$ bond length 2.140(9)Å was also similar to the Os–$N_{pyridine}$ bond lengths in *trans*-Os(η^4-CHBA-Et)(py)$_2$ (2.105(3)Å ave.). The Os–Cl bond length was 2.344(3)Å. A complete listing of bond lengths and bond angles are given in Tables 1.10 and 1.11.

Figure 1.15. ORTEP view of *trans*-Os(η^2-HBA-TMI)$_2$Cl$_2$. Bond lengths are in angstroms and bond angles are in degrees.

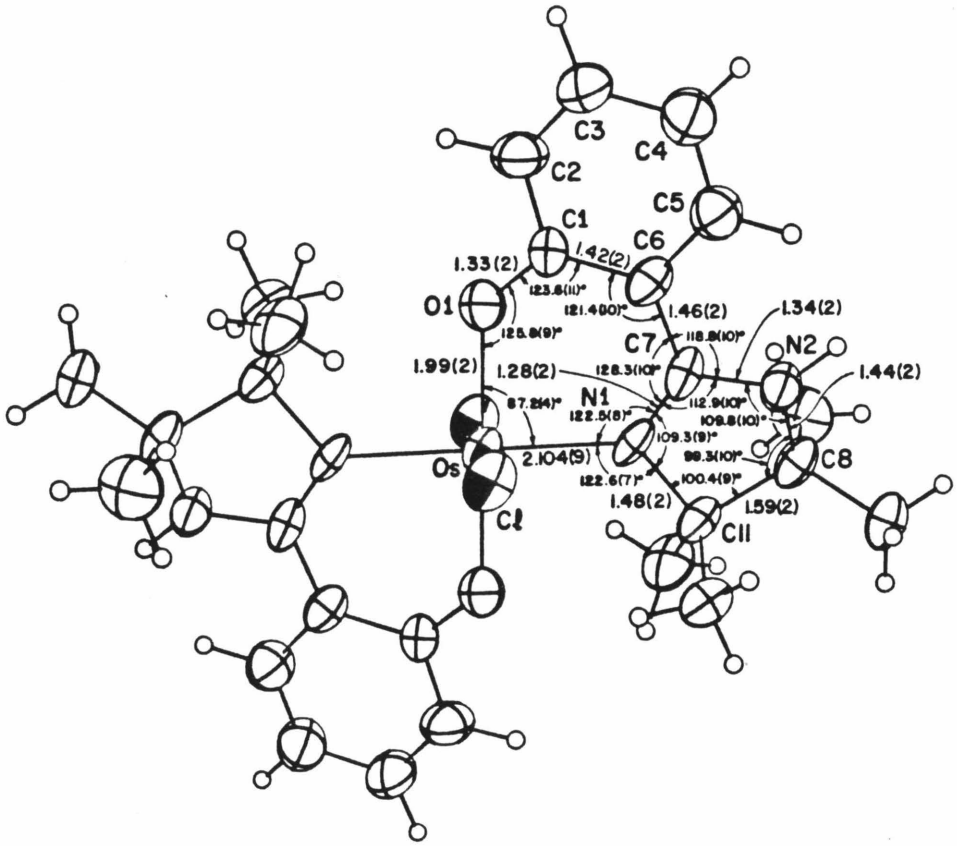

C3
C4
C2
C5
C1
C6
1.33(2)
1.42(2)
123.8(11)°
121.4(10)°
O1
1.46(2)
1.34(2)
125.8(9)°
C7
118.8(10)°
N2
1.99(2)
1.28(2)
128.3(10)°
1.44(2)
87.2(4)°
N1
122.5(8)°
112.9(10)°
109.8(10)°
109.3(9)°
99.3(10)°
C8
Os
2.104(9)
122.6(7)°
100.4(9)°
1.48(2)
1.59(2)
Cl
C11

Table 1.10. Bond lengths (in angstroms) for the molecular structure of *trans*-$Os(\eta^2\text{-(H)HBA-TMI})_2Cl_2$.

Cl	Os	2.343(3)
O1	Os	1.99(2)
N1	Os	2.104(9)
O1	C1	1.33(2)
C1	C2	1.41(2)
C2	C3	1.35(2)
C3	C4	1.41(2)
C4	C5	1.39(2)
C5	C6	1.41(2)
C1	C6	1.42(2)
C6	C7	1.46(2)
N1	C7	1.28(2)
N2	C7	1.34(2)
N2	C8	1.44(2)
C8	C11	1.59(2)
N1	C11	1.48(2)
C8	C9	1.51(2)
C8	C10	1.56(2)
C11	C12	1.53(2)
C11	C13	1.57(2)

Table 1.11. Bond angles (in degrees) for the molecular structure of *trans*-Os(η^2-(H)HBA-TMI)$_2$Cl$_2$.

O1 – Os –Cl	91.9(4)
O1 – Os –Cl	88.1(4)
N1 – Os –Cl	89.3(3)
N1 – Os –Cl	90.7(3)
N1 – Os –O1	87.2(4)
Os – O1 –C1	125.8(9)
C6 – C1 –O1	123.6(11)
C2 – C1 –O1	118.0(16)
C2 – C1 –C6	118.2(11)
C1 – C2 –C3	122.9(14)
C2 – C3 –C4	120.6(16)
C3 – C4 –C5	116.9(15)
C4 – C5 –C6	124.0(13)
C1 – C6 –C5	117.3(11)
C1 – C6 –C7	121.4(10)
C5 – C6 –C7	121.2(11)
C6 – C7 –N1	128.3(10)
C6 – C7 –N2	118.8(10)
N1 – C7 –N2	112.9(10)
Os – N1 –C7	122.5(8)
Os – N1 –C11	122.6(7)
C7 – N1 –C11	109.3(9)
C7 – N2 –C8	109.8(10)
C9 – C8 –N2	113.2(11)
C10– C8 –N2	108.4(12)
C11– C8 –N2	99.3(10)
C9 – C8 –C10	109.0(12)
C9 – C8 –C11	114.7(11)
C10– C8 –C11	111.8(11)
C8 –C11–N1	100.4(9)
C12–C11–N1	113.8(10)
C13–C11–N1	108.3(10)
C8 –C11–C12	112.5(10)
C8 –C11–C13	111.0(11)
C12–C11–C13	110.4(11)

Conclusions

It appears that the utility of the derivatives of 1,2-bis(2-hydroxybenzamido)-ethane as ligands capable of stabilizing transition metals in the higher valent states is limited to systems where *N*-coordination of the organic amide exists. Complexation of these ligands to chromium(III) and iron(III) has most likely resulted in the formation of *O*-bound dimeric and/or polymeric complexes. Only in one instance has *N*-coordination of the organic amide been documented. Oxidation of these trivalent species did not produce tractable high valent compounds. Had monomeric complexes formed, higher valent complexes should have been accessible; $[Cr(salen)(H_2O)_2]PF_6$ is easily oxidized to a stable chromium(V) complex.[16] Compounds such as Os(η^4-CHBA-DCBz)(py)$_2$[†] can be oxidized electrochemically to complexes of osmium(V) and possibly higher valencies;[18] here the coordination is known to be via the deprotonated amide nitrogen atoms and the deprotonated phenolic oxygen atoms. No tractable complexes were found on direct reaction of high valent chromium with these ligands.

X-ray crystallographic studies have complemented the synthetic investigations on the coordination chemistry of these bis-hydroxybenzamido ligands. We have characterized the first examples of *N*-bound organic amide coordination to chromium(III) in a molecule where the ligand bridges two metal centers. Both forms of monodentate organic amide coordination were found and the *N*-bound form was observed to be a stronger σ-donor, as expected.

Coordination to one metal center in a planar fashion was also discovered. An unusual osmium(IV) μ-oxo dimer has been characterized in which potassium ions, in low coordination environments, are thought to lock the structure in a conformation where the large planar chelates are essentially eclipsed. Comparisons of the metrical data with that found for the free ligand, also structurally characterized, indicate few significant differences. The structure of *trans*-Os(η^4-CHBA-HMEt)(py)$_2$ was found to be very similar to that of *trans*-Os(η^4-CHBA-Et)(py)$_2$

[†] CHBA-DCBz = tetraanion of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene.

and in agreement with the solution NMR spectroscopic data.[18] These structural studies have provided a foundation for the production of solution-stable highly oxidized complexes with formal potentials as high as 2.5 volts.[18,46]

The rearrangement of $(H)_4$HBA-DMBu in the presence of $(NH_4)_2OsCl_6$ at temperatures greater than 300°C has resulted in an unusual osmium(IV)-imidazoline complex. These imidazoline ligands may also be useful chelates for stabilizing metal ions in high oxidation states.[47]

Experimental

General Information

Physical and Spectroscopic Methods. Proton NMR spectra were recorded on a Varian 390 spectrometer. The chemical shifs are reported in ppm(δ) relative to tetramethylsilane (δ = 0.0). Infrared spectra were obtained using a Beckman 4240 spectrometer; nujol mulls were routinely used with potassium bromide plates unless noted otherwise. All infrared spectral assignments are tentative. No NMR spectra were obtained for the chromium(III) and iron(III) complexes, due to their paramagnetic nature, thus unambiguous characterization has been difficult.

Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Galbraith Laboratories, Inc., or by Mr. L. Henling at the C.I.T. Chemistry Dept. Analytical Facility. Magnetic susceptibilities were measured on a Cahn Electrobalance, model DTL, which employs the Faraday Technique.

Materials. All solvents were reagent grade and used without further purification, except for dichloromethane and tetrahydrofuran which were freshly distilled from calcium hydride.

The following compounds were used as received: 2-acetylsalicylic acid, *t*-butyl hydroperoxide, *m*-chloroperbenzoic acid, chromyl chloride, *sym*-dimethylethylenediamine, ethylenediamine, *o*-phenylenediamine (all from the Aldrich Chemical Co.), chromium trichloride hexahydrate, chromium trioxide, anhydrous ferric chloride, hydrogen peroxide, anhydrous sodium carbonate, sodium hydroxide (all from Baker Chemical Co.), cerric ammonium nitrate, hydrochloric acid, *meta*-sodium periodate, triethylamine (all from Mallinckrodt Inc.), 3,5-dichlorosalicylic acid, iodosylbenzene (from Pfaltz and Bauer Chemical Co.), trichlorotris(tetrahydrofuran)chromium(III) (from Alfa Chemical Co.), and chlorine gas from the Matheson Co. Oxalyl chloride from both Pfaltz and Bauer Chemical Co. and the Aldrich Chemical Co. was freshly distilled before use.

The following compounds were synthesized using reported procedures: 2-acetyl-5-*t*-butylsalicylic acid,[48] 2-acetyl-3,5-dichlorosalicylic acid,[49] 2,3-diamino-2,3-dimethylbutane,[50] Cr(O-*t*-Bu)$_4$,[51] and Na[CrO(O$_2$CC(CH$_3$)$_2$O)$_2$].[52]

Synthesis

Preparation of $(H)_4$HBA-Et. 2-acetylsalicylic acid (50.0 g,0.277 mol) was mixed with 50–60 mL of neat oxalyl chloride in a 250 mL round bottom flask. The reaction flask was vented to a hood and maintained at 30°C for 4 hours. The initial slurry gradually changes to a pale yellow solution as the acid was converted to the acid chloride. When the gas evolution had ceased, the remaining oxalyl chloride was distilled off ***in vacuo***. The residue was dissolved in 30 mL of dry dichloromethane which was also distilled off ***in vacuo***; this step was repeated several times to remove the last traces of oxalyl chloride. The residue was dissolved in 100 mL of dry dichloromethane and refrigerated. A solution of ethylenediamine (9.277 mL,0.138 mol) and 100 mL of dry dichloromethane was placed in a 500 mL round bottom flask equipped with a stir bar. After the solution had cooled sufficiently in an ice bath, the freshly prepared acid chloride solution was slowly dripped in with stirring. The slurry was stirred for 1 hour at which time an excess of 1 equivalent of triethylamine was added; the mixture was stirred for an additional $\frac{1}{2}$ hour. This mixture was then treated with *ca.* 100 mL of warm 6M NaOH and heated ***in vacuo*** to distill off the dichloromethane and triethylamine. The remaining aqueous solution was decanted from the undissolved organic residues which were then dissolved in a minimal amount of acetone and treated with an additional 50 mL of warm 6M NaOH. The acetone was then distilled off ***in vacuo*** and the aqueous portions were combined. This very basic solution was cooled on ice, and was then cautiously acidified with concentrated HCl. The product precipitated and was easily collected. The recrystallized yield (from acetone/water) was 33.3 g (80%).

Tentative analytical data: $(H)_4$HBA-Et

IR (cm^{-1},nujol): 3418 [ss,ν(NH)], 1647 [ss,ν(CO)].

^{1}H NMR (acetone-d_6): 6.61–7.68 [m,8H,Ph], 3.21–3.68 [m,4H,CH_2].

E.A.: (Calc.) C: 63.99%, H: 5.37%, N: 9.32%;

(Found) C: 64.12%, H: 5.58%, N: 9.14%.

χ_m (cgs units): -192×10^{-6}.

Preparation of $(H)_4$HBA-*o*Bz, $(H)_4$HBA-DMBu, $(H)_4$*t*BuHBA-Et, $(H)_4$CHBA-*o*Bz[†], and $(H)_2$*N*MHBA-Et. These compounds: 1,2-bis(2-hydroxybenzamido)-benzene, 2,3-bis(2-hydroxybenzamido)-2,3-dimethylbutane, 1,2-bis(5-*t*-butyl-2-hydroxybenzamido)ethane, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)benzene, and 1,2-bis(*N*-methyl-2-hydroxybenzamido)ethane, were all synthesized in an analogous manner to that of 1,2-bis(2-hydroxybenzamido)ethane, described above. Table 1.12 lists the starting materials, recrystallizing solvents, and yields for these preparations.

Tentative analytical data: $(H)_4$HBA-*o*Bz
IR (cm^{-1},nujol): 3383 [ms,ν(NH)], 1638 [sh,ν(CO)].
^{1}H NMR (acetone-d_6): 7.63–8.10 [m,4H,Ph], 7.23–7.53 [m,4H,Ph], 6.76–7.00 [m,4H,Ph].
E.A.: (Calc.) C: 68.96%, H: 4.63%, N: 8.04%;
(Found) C: 69.04%, H: 4.75%, N: 8.14%.
χ_m (cgs units): -124×10^{-6}.

Tentative analytical data: $(H)_4$HBA-DMBu
IR (cm^{-1},nujol): 3359 [ms,ν(NH)], 1625 [sh,ν(CO)].
^{1}H NMR (acetone-d_6): 7.83–8.00 [m,2H,Ph], 7.25–7.50 [m,2H,Ph], 6.76–7.00 [m,4H,Ph], 1.65 [s,12H,CH_3].
E.A.: (Calc.) C: 67.40%, H: 6.79%, N: 7.86%;
(Found) C: 67.37%, H: 6.86%, N: 7.68%.
χ_m (cgs units): -214×10^{-6}.

Tentative analytical data: $(H)_4$*t*BuHBA-Et
IR (cm^{-1},nujol,NaCl plates): 3365 [ms,ν(NH)], 1648 [ss,ν(CO)].
^{1}H NMR (acetone-d_6): 7.79 [d,2H,Ph], 7.40–7.56 [m,2H,Ph], 6.82 [d,2H,Ph], 3.64 [s,4H,CH_2], 1.30 [s,18H,*t*Bu].
E.A.: (Calc.) C: 69.88%, H: 7.82%, N: 6.79%;
(Found) C: 70.13%, H: 8.05%, N: 6.63%.
χ_m (cgs units): -237×10^{-6}.

Tentative analytical data: $(H)_4$CHBA-*o*Bz

[†] Direct chlorination of $(H)_4$HBA-*o*Bz was not productive.

Table 1.12. Pertinent data for the syntheses of the organic chelates: $(H)_4$HBA-*o*Bz, $(H)_4$HBA-DMBu, $(H)_4$*t*BuHBA-Et, $(H)_4$CHBA-*o*Bz, $(H)_2$*N*MHBA-Et.

Ligand	Starting Materials	Recrystallizing Solvents	Yield
$(H)_4$HBA-*o*Bz	2-acetylsalicylic acid; *o*-phenylene-diamine	acetone/ water	81%
$(H)_4$HBA-DMBu	2-acetylsalicylic acid; 2,3-diamino-2,3-dimethylbutane	DMF/ water	56%
$(H)_4$*t*BuHBA-Et	5-*t*-butyl-2-acetyl-salicylic acid; ethylenediamine	acetone/ water	50%
$(H)_4$CHBA-*o*Bz	2-acetyl-3,5-dichloro-salicylic acid; *o*-phenylene diamine	acetone/ water	75%
$(H)_2$*N*MHBA-Et	2-acetylsalicylic acid; *sym*-*N*,*N*'-dimethyl-ethylenediamine	DMF/ water	66%

IR (cm^{-1},nujol): 3385 [mb,ν(NH)], 1646 [ss,ν(CO)].
^{1}H NMR (acetone-d_6): 8.00 [d,2H,Ph], 7.68–7.50 [m,4H,Ph], 7.10–7.30 [m,2H,Ph].
E.A.: (Calc.) C: 49.41%, H: 2.49%, N: 5.76%;
(Found) C: 49.52%, H: 2.68%, N: 5.85%.

Tentative analytical data: $(H)_4$*N*MHBA-Et
IR (cm^{-1},nujol): 1570 [sb,ν(CO)].
^{1}H NMR ($CDCl_3$): 6.7–7.5 [m,8H,Ph], 4.1[s(br),4H,CH_2], 3.2 [s(br),6H,*N*-CH_3].
E.A.: (Calc.) C: 65.84%, H: 6.14%, N: 8.53%;
(Found) C: 65.45%, H: 6.09%, N: 8.49%.

Preparation of $(H)_4$CHBA-Et. $(H)_4$HBA-Et (5 g) is dissolved in 80–100 mL of warm glacial acetic acid in a 500 mL filtration flask. Chlorine gas was bubbled through the solution for $\frac{1}{2}$ hour period; the product precipitated during this time due to its low solubility in acetic acid. The mixture was then cooled on ice. The product was collected on a glass frit and washed with cold water. It was then recrystallized from acetone/water. The overall yield was 6.6 g (90%).

Tentative analytical data: $(H)_4$CHBA-Et[18]
IR (cm^{-1},nujol): 3343 [ss,ν(NH)], 1632 [ss,ν(CO)].
^{1}H NMR (acetone-d_6): 7.76 [d,2H,Ph], 7.58 [d,2H,Ph], 3.70 [s,4H,CH_2].
χ_m (cgs units): -192×10^{-6}.

Preparation of $\{Na[Cr(\eta^4\text{-}(H)_2HBA\text{-}Et)(OH)_2]\}_x$. $CrCl_3 \cdot 6H_2O$ (444 mg,0.0017 mol) was dissolved in *ca.* 50 mL of *N,N'*-dimethylformamide and heated under reflux in a 100 mL beaker. The ligand, $(H)_4$HBA-Et (500 mg,0.0017 mol) was then added to the solution which was stirred for 2 minutes. At this point the heat was reduced and a large amount (*ca.* 5 g) of anhydrous sodium carbonate was mixed into the solution. After stirring for an additional 2 minutes, the mixture was filtered and cooled to room temperature. The product formed on addition of

acetone. It was filtered from the solution, washing with diethyl ether, and dried *in vacuo*. The yield was approximately 75% (0.52 g).

Tentative analytical data: $\{Na[Cr(\eta^4\text{-}(H)_2HBA\text{-}Et)(OH)_2]\}_x$
IR (cm^{-1},nujol): 3100–3650 [br,ν(OH);obscured,ν(NH)], 1610 [ss,ν(CO)].
E.A.: (Calc.) C: 47.18%, H: 3.96%, N: 6.88%;
(Found) C: 46.97%, H: 4.08%, N: 6.70%.
μ_{eff} (Bohr magnetons): (Calc.) 3.87; (Found) 3.70.

Preparation of $\{Na[Cr(\eta^4\text{-}(H)_2CHBA\text{-}Et)(OH)_2]\}_x$. $CrCl_3 \cdot 6H_2O$ (304 mg, 0.0011 mol) was dissolved in *ca.* 100 mL of acetone and heated under reflux in a 100 mL beaker. When the salt had completely dissolved, $(H)_4$CHBA-Et (500 mg,0.0011 mol) was added, changing the color from purple to khaki. After 2 minutes the heat was reduced and anhydrous sodium carbonate (*ca.* 5 g) was mixed into the solution. After stirring for an additional 2 minutes, the mixture was filtered and cooled to room temperature. Upon the addition of diethyl ether, the product precipitated. It was filtered from the solution, washed with diethyl ether, and dried *in vacuo*. The yield was approximately 85% (0.51 g).

Tentative analytical data: $\{Na[Cr(\eta^4\text{-}(H)_2CHBA\text{-}Et)(OH)_2]\}_x$
IR (cm^{-1},nujol): 3100–3650 [br,ν(OH);obscured,ν(NH)], 1595 [ss,ν(CO)].
E.A.: (Calc.) C: 35.26%, H: 2.22%, N: 5.14%;
(Found) C: 35.11%, H: 2.60%, N: 5.16%.
μ_{eff} (Bohr magnetons): (Calc.) 3.87; (Found) 3.86.

Preparation of $\{Na[Cr(\eta^4\text{-}(H)_2HBA\text{-}o\text{Bz})(OH)_2]\}_x \cdot 3xH_2O$. The procedure for this synthesis is analogous to that of $\{Na[Cr(\eta^4\text{-}(H)_2HBA\text{-}Et)(OH)_2]\}_x$, as described above. Using 382 mg (0.0014 mol) of $CrCl_3 \cdot 6H_2O$ and 500 mg (0.0014 mol) of $(H)_4$HBA-*o*Bz (in *ca.* 50 mL *N,N'*-dimethylformamide), the complex was isolated in 80% yield (0.57 g).

Tentative analytical data: $\{Na[Cr(\eta^4\text{-}(H)_2HBA\text{-}oBz)(OH)_2]\}_x \cdot 3xH_2O$*
IR (cm^{-1},nujol): 3000–3650 [br,ν(OH);obscured,ν(NH)], 1610 [ss,ν(CO)].
E.A.: (Calc.) C: 47.16%, H: 4.35%, N: 5.50%;
(Found) C: 47.20%, H: 4.03%, N: 5.44%.
μ_{eff} (Bohr magnetons): (Calc.) 3.87; (Found) 4.01.

Preparation of $\{Cr((H)CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$. $CrCl_3 \cdot 6H_2O$ (304 mg,0.0011 mol) was dissolved in *ca.* 50 mL of pyridine and heated under reflux in a 100 mL beaker. When the salt was dissolved, $(H)_4$CHBA-Et was added to the hot solution. After 2 minutes approximately 5 g of anhydrous sodium carbonate were mixed into the solution. The mixture was stirred for an additional 2 minutes and then filtered. The dark green solution was placed in a sealed bottle and set aside in a cool dark place. After several weeks green crystals formed; a pale green powder also precipitated. The yield of crystals collected was estimated at 5%. Infrared spectra of the crystals and the amorphous material were found to be the same.

Tentative analytical data: $\{Cr((H)CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$
IR (cm^{-1},nujol): 3150–3300 [br,ν(NH)], 1508 [ss,ν(CO)].
X-ray crystallographic analysis described below.

Preparation of crude $\{Na[Cr(\eta^4\text{-}N\text{MHBA-Et})(OH)_2]\}_x$. The synthesis of this impure complex is similar to that of $\{Na[Cr(\eta^4\text{-}(H)_2HBA\text{-Et})(OH)_2]\}_x$. $CrCl_3 \cdot 6H_2O$ (406 mg,0.0015 mol) and 500 mg (0.0015 mol) of $(H)_2N$MHBA-*o*Bz were dissolved in acetone (*ca.* 50 mL) and heated under reflux. After 2 minutes the heat was reduced and anhydrous sodium carbonate (*ca.* 5 g) was mixed into the solution. The mixture was stirred for an additional 2 minutes, then filtered and cooled to room temperature. Upon the addition of tetrahydrofuran, the product precipitated. It was then filtered from the solution and dried *in vacuo*.

* No independent verification for the waters of hydration.

Tentative analytical data: $\{Na[Cr(\eta^4\text{-}(H)_2NMHBA\text{-}Et)(OH)_2]\}_x$
IR (cm^{-1},nujol): 3100–3650 [br,ν(OH)], 1609 [ss,ν(CO)].

Preparation of $\{Na[Fe(\eta^4\text{-}(H)_2HBA\text{-}Et)(OH)_2]\}_x \cdot xH_2O$. The procedure for this synthesis is analogous to that of $\{Na[Cr(\eta^4\text{-}(H)_2HBA\text{-}Et)(OH)_2]\}_x$, as described above. Using 270 mg (0.0017 mol) of $FeCl_3$ and 500 mg (0.0017 mol) of $(H)_4$HBA-Et (in *ca.* 50 mL *N,N'*-dimethylformamide), the complex was isolated in 75% yield (0.55 g).

Tentative analytical data: $\{Na[Fe(\eta^4\text{-}(H)_2HBA\text{-}Et)(OH)_2]\}_x \cdot xH_2O$[§]
IR (cm^{-1},nujol): 3100–3650 [br,ν(OH),obscured,ν(NH)], 1610 [ss,ν(CO)].
E.A.: (Calc.) C: 44.78%, H: 4.23%, N: 6.53%;
(Found) C: 44.40%, H: 3.97%, N: 6.54%.
μ_{eff} (Bohr magnetons): (Calc.) 5.92; (Found) 4.37.

Preparation of crude $\{Na[Fe(\eta^4\text{-}(H)_2CHBA\text{-}Et)(OH)_2]\}_x$ and $\{Na[Fe(\eta^4\text{-}(H)_2HBA\text{-}o\text{Bz})(OH)_2]\}_x$. Compounds of iron containing the ligands $(H)_4$CHBA-Et and $(H)_4$HBA-*o*Bz were made under the same conditions as their chromium analogues. Elemental analyses of these complexes indicate they were not pure.

Tentative analytical data: $\{Na[Fe(\eta^4\text{-}(H)_2CHBA\text{-}Et)(OH)_2]\}_x$
IR (cm^{-1},nujol): 3100–3650 [br,ν(OH);obscured,ν(NH)], 1600 [ss,ν(CO)].

Tentative analytical data: $\{Na[Fe(\eta^4\text{-}(H)_2HBA\text{-}o\text{Bz})(OH)_2]\}_x$
IR (cm^{-1},nujol): 3100–3650 [br,ν(OH);obscured,ν(NH)], 1608 [ss,ν(CO)].

Oxidations of trivalent complexes. The metal complexes were freshly prepared, as described above, except that they were not precipitated from the filtered solution. These solutions were heated under reflux and then an excess of one equivalent of the oxidant (hydrogen peroxide, *m*-chloroperbenzoic acid, iodosylbenzene, *meta*-sodium periodate, or *t*-butyl hydroperoxide) was added; no

§ No independent verification for the waters of hydration.

apparent reaction occurred at room temperature. The solutions usually changed to a dark brown color within three minutes. After cooling to room temperature, the products were precipitated (by the addition of diethyl ether) and filtered from the solution. The materials were then washed with diethyl ether and dried *in vacuo*. Infrared spectroscopic data and elemental analyses indicated the trivalent complexes were not cleanly oxidized to higher valent compounds.

Reactivity of $(H)_4$CHBA-Et *with* CrO_3, CrO_2Cl_2, $Na[CrO(O_2C(CH_3)_2O)_2]$, and $Cr(O\text{-}t\text{-}Bu)_4$. Direct reactions of chromium trioxide or chromyl chloride (1 equiv.) with $(H)_4$CHBA-Et (1 equiv.) were not productive; intractable powders were isolated under a variety of conditions, *e.g.*, in acetone, *N,N*-dimethylformamide, tetrahydrofuran, or dichloromethane, with and without heating, and with and without added sodium carbonate or other bases. No reaction was observed between $(H)_4$CHBA-Et and $Na[CrO(O_2C(CH_3)_2O)_2]$ in acetone. An intractable gray-green powder resulted on mixing $(H)_4$CHBA-Et (1 equiv.) with $Cr(O\text{-}t\text{-}Bu)_4$ (1 equiv.) in dry degassed tetrahydrofuran.

X-ray Crystallography[†]

Structure Determination of $(H)_4$CHBA-Et·pyHCl.

Data collection. A crystal roughly 0.25 mm on a side was mounted on a glass fiber with epoxy. Oscillation and Weissenberg photographs indicated that the space group was of the monoclinic class. The intensity data were collected on a locally modified Syntex $P2_1$ diffractometer with MoK_α radiation ($\lambda = 0.7107$Å) and a graphite monochromator.

Unit cell parameters were obtained by least-squares refinement of the orientation matrix using 15 centered reflections in the range $19° < 2\theta < 38°$: a = 10.659(3)Å, b = 22.472(6)Å, c = 4.890(2)Å, $\beta = 95.63(2)°$, and V = 1165.8(6)Å^3. The systematic absences led to the assignment of the space group $P2_1$ (0k0: k=odd, h0l: none, hkl: none).

A total of 6033 intensity measurements were recorded for reflections in one hemisphere ($3.5° < 2\theta < 46.0°$) using θ-2θ scans at a constant scan speed of 4.88°/min ($2\theta \leq 36.0°$) or 3.91°/min ($2\theta > 36.0°$). Background measurements were recorded for a time interval equal to half the scan time before and after each scan. The integrated intensities were calculated in the following manner: $I = R[C - T(B_1 + B_2)]$, where R is the scan rate, C is the scan count, B_1 and B_2 are the background measurements, and T is the ratio of the scan time to the total background counting time. Three check reflections were remeasured after every 197 reflections. No decay was observed; absorption corrections were not applied. Observational variances, $\sigma^2(F_o^2)$, were based on counting statistics plus a term, 0.02C, where C is the scan count. After deletion of systematic absences, and averaging of multiple and symmetry-related reflections, the total number of unique data was 2892 of which 2268 were greater that 3σ.

Structure determination and refinement. The atomic positions of the chlorine atoms were generated by MULTAN.[54] Subsequent Fourier and difference

[†] All calculations were carried out on VAX 11/780 and VAX 11/750 computers using the CRYRM crystallographic system.[53]

Fourier maps revealed all non-hydrogen atoms. Atomic scattering factors were taken from Stewart, Davidson, and Simpson[55] for H and the *International Tables for X-ray Crystallography*[56] for all others.

Several cycles of full-matrix least-squares refinement minimizing $\sum w\left(F_o^2 - (F_c/k)^2\right)^2$, $w = \sigma^{-2}(F_o^2)$, on all non-hydrogen parameters yielded $R = \left\{\sum ||F_o| - |F_c/k||/|F_o|\right\} = 0.192$ and $GOF = \left\{\sum w\left(F_o^2 - (F_c^2/k)\right)^2/(n_o - n_p)\right\}^{\frac{1}{2}} = 3.62$, where n_o is the number of reflections and n_p is the number of parameters; all atomic coordinates were in one block and the scale factor and the isotropic Gaussian ellipsoids were in the other. Subsequently, the Gaussian ellipsoids were refined anisotropically and hydrogen atoms on the carbon and nitrogen atoms were placed a distance of 1.0Å from them by assuming ideal geometry; phenolic hydrogen atoms were found on a difference Fourier map. Hydrogen atom coordinates and isotropic thermal parameters (B = 5.0Å) were not refined. The final cycle of least-squares refinement gave values for R and $R_{3\sigma}$, the R-factor calculated using only the reflections with $F_o^2 > 3\sigma(F_o^2)$, of 0.045 and 0.034; the GOF was 1.51 and the data-to-parameter ratio was 7.99. The final values for the atomic coordinates and Gaussian ellipsoids are given in Table 1.13.

Structure determination of $\{Cr((H)CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$.

Data Collection. Oscillation photographs of crystals large enough for *X*-ray analysis indicated that most were badly twinned. One crystal, however, was found to extinguish well under polarized light. An oscillation photograph revealed that the individual selected for intensity data collection was a single crystal with only a minor twin component. The crystal, roughly a cube 0.25 mm on a side, was mounted on a glass fiber with epoxy. The intensity data were collected on the locally modified Syntex $P2_1$ automated diffractometer with MoK_α radiation (λ = 0.7107Å) and a graphite monochromator.

Unit cell parameters were obtained by least-squares refinement of the orientation matrix using 15 centered reflections in the range $18° < 2\theta < 35°$: a = 14.343(4)Å, b = 14.225(3)Å, c = 16.447(8)Å, β = 104.28(3)°, and V = 3252(2)Å^3.

Table 1.13. Fractional coordinates (CLA–P5: $\times 10^5$; HO1–HP5: $\times 10^4$) and thermal parameters ($U_{ij} \times 10^4$ in Å^2; B in Å^2) for $(H)_4$CHBA-Et·pyHCl.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
CLA	45154(11)	8060(08)	24070(25)	428(06)	504(07)	501(07)	-103(06)	69(05)	-124(06)
CLB	34880(12)	24880(00)	96448(30)	400(07)	519(08)	646(10)	102(06)	196(07)	-148(07)
CLC	125281(13)	-16124(08)	27226(28)	607(08)	527(07)	633(09)	139(07)	76(07)	-176(07)
CLD	88973(12)	-16231(08)	95995(31)	495(07)	509(08)	908(10)	-134(07)	139(07)	161(08)
O1	620331(29)	24820(14)	112248(63)	467(18)	333(16)	522(18)	3(15)	99(15)	-146(15)
O2	126871(30)	-3413(15)	39443(66)	423(19)	480(18)	537(19)	5(15)	168(16)	-21(15)
O3	84254(29)	20955(14)	110611(67)	407(18)	480(20)	534(21)	16(15)	-10(16)	-160(16)
O4	121771(33)	5830(14)	64957(71)	556(23)	433(19)	770(24)	-139(17)	379(20)	-113(17)
N1	89355(32)	15804(17)	73582(74)	273(18)	481(22)	447(23)	19(16)	27(17)	-84(18)
N2	106728(34)	6054(16)	93768(73)	329(20)	406(22)	511(22)	-25(16)	130(17)	-74(17)
C1	58647(39)	20966(18)	91617(85)	378(24)	280(21)	423(24)	7(18)	122(20)	27(18)
C2	45803(41)	20481(19)	81496(97)	352(24)	335(230	564(30)	68(20)	133(22)	-21(21)
C3	41592(42)	16606(20)	61277(94)	342(25)	396(25)	485(25)	1(20)	85(21)	64(20)
C4	50437(41)	13101(19)	49937(86)	389(24)	301(22)	417(25)	-35(18)	87(20)	-1(18)
C5	63133(40)	13495(19)	58329(88)	352(23)	335(22)	426(24)	20(18)	68(19)	12(18)
C6	67303(38)	17450(19)	79071(87)	289(21)	325(22)	369(24)	14(18)	66(19)	3(18)
C7	80989(42)	18153(19)	89068(90)	405(24)	284(23)	436(26)	38(19)	41(20)	26(19)
C8	102944(39)	16688(20)	80254(94)	326(21)	430(26)	471(29)	-33(20)	73(20)	-65(22)
C9	108921(40)	12264(20)	101659(92)	346(25)	389(22)	557(28)	-4(20)	27(22)	-94(20)
C10	113444(38)	3225(21)	76480(87)	312(21)	409(23)	456(26)	-24(20)	56(19)	-1(22)
C11	110926(39)	-3193(18)	71073(85)	302(23)	341(22)	386(26)	31(18)	16(19)	-8(19)
C12	101890(41)	-6362(21)	84416(90)	360(24)	442(26)	489(27)	-2(20)	72(21)	45(22)
C13	100147(42)	-12346(22)	79067(97)	373(25)	423(26)	512(29)	-57(21)	20(22)	60(23)
C14	107306(43)	-15389(21)	61970(97)	465(25)	400(27)	571(28)	38(22)	-68(22)	-1(23)
C15	116109(43)	-12282(20)	48824(88)	447(27)	413(24)	427(26)	106(22)	18(21)	-35(20)
C16	118120(40)	-6212(20)	53027(86)	327(23)	408(25)	426(26)	27(19)	2(20)	18(20)
PCL	83730(12)	3529(08)	28833(27)	476(07)	507(07)	672(08)	-4(06)	292(06)	-37(06)
PN	33099(43)	45919(21)	39569(94)	522(26)	596(26)	609(26)	100(21)	-3(22)	-176(22)
P1	34094(54)	40493(27)	50095(110)	654(37)	784(39)	580(35)	-132(32)	64(29)	-86(29)
P2	42792(60)	36680(25)	41453(114)	881(47)	461(32)	588(36)	-56(32)	-87(33)	-14(29)
P3	50547(52)	38532(24)	22123(108)	559(33)	532(32)	622(34)	133(27)	-32(28)	-93(27)
P4	49365(52)	44150(24)	12164(105)	545(33)	605(33)	603(32)	33(27)	99(27)	-65(26)
P5	40484(57)	47824(23)	21051(111)	764(39)	456(31)	595(34)	69(27)	60(30)	-22(25)

Atom	x	y	z	B
HO1	7130	2470	11590	5.0
HO2	12922	77	4490	5.0
HN1	8628	1324	5701	5.0
HN2	9978	360	10238	5.0
HC3	3222	1632	5424	5.0
HC5	6940	1088	4935	5.0
HC8A	10425	2090	8781	5.0
HC8B	10738	1640	6314	5.0
HC9A	10529	1304	11958	5.0
HC9B	11823	1295	10423	5.0
HC12	9671	-423	9809	5.0
HC14	10603	-1975	5834	5.0
HPN	2653	4871	4683	5.0
HP1	2817	3919	6368	5.0
HP2	4310	3257	4967	5.0
HP3	5775	3578	1633	5.0
HP4	5496	4560	-285	5.0
HP5	4107	5162	1052	5.0

The systematic absences led to the assignment of the space group $P2_1/c$ (0k0: k=odd, h0l: l=odd, hkl: none).

A total of 8370 intensity measurements were recorded for reflections in one hemisphere ($4.0° < 2\theta < 45.0°$) using θ-2θ scans at a constant scan speed of 2.02°/min with a fixed symmetric scan width of 2.0° in 2θ. Background measurements were recorded for approximately 30 seconds[‡] before and after each scan. The integrated intensities were calculated in the following manner: $I = R[C - T(B_1 + B_2)]$, where R is the scan rate, C is the scan count, B_1 and B_2 are the background measurements, and T is the ratio of the scan time to the total background counting time. Three check reflections were remeasured after every 97 reflections. A linear least-squares fit of intensities of these check reflections implied a 5% decay over the 206 hours of data collection. Absorption corrections were deemed unnecessary ($\mu = 7.4\ cm^{-1}$). Observational variances, $\sigma^2(F_o^2)$. were based on counting statistics plus a term, 0.02C, where C is the scan count. After deletion of systematic absences, and averaging of multiple and symmetry-related reflections, the total number of unique data was 3685 of which 2031 were greater that 3σ.

Structure determination and refinement. The atomic positions of the chromium atoms were derived from the Patterson map. Subsequent Fourier and difference Fourier maps revealed all non-hydrogen atoms. Atomic scattering factors were taken from Stewart, Davidson, and Simpson[55] for H, and the *International Tables for X-ray Crystallography*[56] for all others.

Several cycles of full-matrix least-squares refinement minimizing $\sum w(F_o^2 - (F_c/k)^2)^2$, $w = \sigma^{-2}(F_o^2)$, on all non-hydrogen parameters yielded $R = \{\sum ||F_o| - |F_c/k||/|F_o|\} = 0.127$ and $GOF = \{\sum w(F_o^2 - (F_c^2/k))^2/(n_o - n_p)\}^{\frac{1}{2}} = 1.76$, where n_o is the number of reflections and n_p is the number of parameters; all atomic coordinates were in one block and the scale factor and the Gaussian ellipsoids (anisotropic for all atoms except those of the disordered pyridine ring)

‡ The background counting time was proportional to $\frac{1}{2}$ the scan time.

were in the other. Hydrogen atoms were placed a distance of 0.99Å from their respective carbon or nitrogen atom by assuming ideal geometry, and were not refined. The final cycle of least-squares refinement gave values for R and $R_{3\sigma}$, the R-factor calculated using only the reflections with $F_o^2 > 3\sigma(F_o^2)$, of 0.122 and 0.055; the GOF was 1.38 and the data-to-parameter ratio was 9.8. The final values for the atomic parameters are given in Table 1.14.

Structure Determination of $K_2[\{Os(\eta^4\text{-CHBA-Et})(OPPh_3)\}_2O]\cdot\frac{5}{2}$acetone$\cdot H_2O$.

Data collection. A dark blue crystal (0.2×0.2×0.2 mm) was mounted on a glass fiber with epoxy. Oscillation and Weissenberg photographs were used to determine the space group for the structure: $P2_1/c$ (h0l: l=odd, 0k0: k=odd, hkl: none). The intensity data was collected on the locally modified Syntex $P2_1$ diffractometer with MoK_α radiation (λ = 0.7107Å) and a graphite monochromator. Lattice parameters were obtained by least-squares refinement of the orientation matrix using fifteen centered reflections ($11.5° < 2\theta < 26.0°$): a = 18.72(1)Å, b = 15.290(9)Å, c = 28.24(2)Å, β = 107.49(5)°, V = 7709(9)Å^3.

A total of 6065 intensity measurements were recorded (+h,+k,±l; $2\theta \leq 36°$) using θ-2θ scans at a constant scan speed of 6°/min with a fixed symmetric scan width of 2.0° in 2θ. Stationary-counter/-crystal background counts were recorded for approximately 30 s before and after each scan. The integrated intensities were calculated in the following manner: $I = R[C - T(B_1 + B_2)]$, where R is the scan rate, C is the scan count, B_1 and B_2 are the background measurements, and T is the ratio of the scan time to the total background counting time. Three check reflections were remeasured after every 97 reflections; a 16% decay in intensity was observed and linear scaling was applied. No absorption corrections were made (μ = 3.98 mm^{-1}). Observational variances, $\sigma^2(F_o^2)$, were based on counting statistics plus a term, 0.02C, where C is the scan count. After deletion of systematic absences, and averaging of multiple and symmetry-related reflections, the total number of unique data was 5331 of which 3411 were greater than 3σ.

Structure determination and refinement. Atomic scattering factors were

Table 1.14. Fractional coordinates (Cr–P10: $\times 10^5$; P11–P16: $\times 10^4$) and thermal parameters ($U_{ij} \times 10^4$ in $Å^2$; B in $Å^2$) for $\{Cr((H)CHBA\text{-}Et)(py)_2\}_2 \cdot 2py$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
CR	31295(07)	-6517(07)	8314(06)	286(06)	313(06)	337(07)	10(06)	64(5)	16(06)
N1	59667(32)	10823(33)	8658(28)	339(32)	380(34)	397(35)	-126(29)	124(28)	-47(29)
N2	73124(31)	3372(31)	659(30)	265(31)	347(33)	395(36)	14(26)	56(26)	29(29)
C1	64166(41)	1804(41)	11777(38)	389(41)	343(40)	505(46)	147(34)	134(37)	177(36)
C2	73941(41)	1130(41)	9487(33)	415(41)	448(42)	193(37)	14(34)	114(32)	71(34)
CA	70844(37)	10902(41)	-16916(38)	210(36)	335(40)	446(47)	38(32)	62(33)	42(37)
CB	74682(39)	16074(42)	-9408(36)	317(39)	404(42)	295(41)	-48(34)	33(33)	8(36)
CC	78632(41)	25027(43)	-9896(39)	496(45)	353(41)	452(48)	-95(39)	38(39)	18(38)
CD	79150(46)	28603(41)	-17404(42)	814(56)	341(44)	422(49)	-242(40)	58(45)	52(39)
CE	75426(45)	23983(45)	-24869(41)	619(47)	403(45)	439(49)	-161(39)	51(40)	74(39)
CF	71402(41)	15371(42)	-24415(36)	497(45)	373(43)	284(43)	-22(37)	24(36)	2(36)
CG	36205(44)	22067(42)	-1229(36)	500(48)	327(45)	403(47)	33(37)	75(39)	68(37)
CH	46421(41)	20762(40)	1540(36)	364(42)	312(40)	353(44)	4(35)	73(35)	72(35)
CI	52770(42)	27581(40)	-131(41)	504(47)	245(43)	573(51)	-42(36)	103(40)	15(38)
CJ	49342(48)	35441(43)	-4546(41)	607(50)	313(45)	601(53)	-114(40)	174(43)	180(39)
CK	39438(51)	36950(45)	-7717(44)	711(55)	338(47)	743(60)	-5(43)	120(48)	107(43)
CM	33358(44)	30360(46)	-6055(40)	528(48)	420(48)	522(51)	57(39)	-8(40)	135(40)
CL1	57390(14)	43776(13)	-6682(13)	882(15)	447(12)	887(16)	-214(12)	230(13)	167(13)
CL2	66426(15)	9575(13)	-33710(11)	1101(17)	535(13)	359(12)	-206(12)	26(11)	-2(10)
CL3	20907(14)	32215(14)	-9724(14)	648(15)	699(15)	1115(20)	118(12)	-8(14)	355(14)
CL4	84290(19)	39825(15)	-17726(13)	1797(25)	682(15)	639(16)	-762(16)	84(16)	70(13)
CO1	50146(42)	11943(41)	6035(35)	426(44)	298(41)	264(40)	-70(37)	70(34)	-20(34)
O1	44768(23)	5344(26)	7483(22)	271(25)	333(26)	378(26)	-7(22)	87(21)	51(23)
CO2	74540(38)	12631(44)	-817(38)	165(36)	547(48)	354(45)	22(37)	34(33)	87(40)
O2	75709(26)	18864(27)	4845(25)	437(28)	418(29)	444(32)	-114(24)	104(24)	-97(24)
O3	66593(25)	2596(26)	-17163(23)	380(27)	321(26)	364(28)	-80(22)	15(23)	47(22)
O4	29613(26)	16348(28)	31(25)	384(28)	420(29)	480(30)	8(23)	72(24)	156(25)
N3	17277(31)	8807(31)	9527(31)	337(34)	320(35)	471(38)	-28(27)	63(29)	6(31)
P1	15117(45)	8244(48)	16913(44)	474(48)	686(57)	666(54)	-55(44)	203(43)	-56(49)
P2	5947(50)	10194(52)	17931(50)	484(52)	805(63)	1050(72)	62(49)	382(50)	-34(54)
P3	-1109(50)	12705(50)	11049(55)	479(54)	772(62)	1131(80)	-33(48)	296(54)	-109(61)
P4	1067(45)	13246(53)	3409(50)	183(41)	903(66)	1018(73)	12(44)	-43(46)	-91(56)
P5	10367(47)	11422(47)	2823(42)	486(49)	552(49)	638(54)	49(42)	58(43)	6(43)
N4	36361(32)	17348(34)	17424(32)	323(34)	371(35)	595(42)	-74(29)	165(31)	-39(32)
P6	32440(44)	25960(48)	16538(42)	538(48)	473(48)	585(54)	54(43)	111(42)	-130(43)
P7	36598(51)	33684(49)	20997(49)	691(58)	483(51)	964(70)	-40(46)	149(52)	-264(51)
P8	45560(52)	32600(49)	26406(48)	688(57)	553(53)	855(64)	-155(49)	218(49)	-296(51)
P9	49699(45)	23713(53)	27440(40)	539(48)	736(57)	461(53)	-56(40)	197(42)	-100(46)
P10	44951(43)	16239(45)	22886(38)	395(41)	500(46)	462(48)	3(39)	150(39)	-5(40)

Atom	x	y	z	B
P11[a]	1101 (06)	3651 (06)	1506 (06)	8.6(0.2)
P12	480 (08)	3856 (07)	748 (07)	10.2(0.3)
P13	-475 (08)	4064 (08)	788 (07)	11.2(0.3)
P14	-718 (07)	3949 (08)	1548 (08)	10.5(0.3)
P15	-117 (10)	3687 (09)	2272 (08)	12.5(0.3)
P16[b]	866 (07)	3564 (07)	2232 (06)	10.4(0.3)

[a] This atom is 0.30 C and 0.70 N.
[b] This atom is 0.70 C and 0.30 N.

taken from Stewart, Davidson. and Simpson[55] for H, and the *International Tables for X-ray Crystallography*[56] for all others. The positions of the osmium atoms were derived from a Patterson map, and the subsequent Fourier and difference Fourier maps indicated the locations of the remaining non-hydrogen atoms; the hydrogen atoms were placed at calculated positions 0.98Å from their respective carbon atom and were not refined. The Gaussian amplitudes of the μ-oxo and the hydrogen atom coordinates (B = 2.75 and 5.0Å^2) and the population of the uncoordinated acetone molecule (set to 0.5) were not refined either.

Full-matrix least-squares refinement minimized the following function: $\sum w\left(F_o^2 - (F_c/k)^2\right)^2$, $w = \sigma^{-2}(F_o^2)$. Subsequent cycles of least-squares led to the final values for $R = \left\{\sum ||F_o| - |F_c/k||/|F_o|\right\} = 0.111$, $R_{3\sigma}$ (the R-factor calculated using only the reflections with $F_o^2 > 3\sigma(F_o^2)$) = 0.076, and $GOF = \left\{\sum w\left(F_o^2 - (F_c^2/k)\right)^2/(n_o - n_p)\right\}^{\frac{1}{2}} = 2.03$, where n_o is the number of reflections and n_p is the number of parameters. All atomic coordinates were in one block and the scale factor and the Gaussian ellipsoids were in the other. The final atomic coordinates and Gaussian thermal parameters appear in Table 1.15.

Structure Determination of *trans*-Os(η^4-CHBA-HMEt)(py)$_2\cdot\frac{1}{4}$H$_2$O.

Data collection. A dark blue crystal (0.1×0.2×0.4 mm) was mounted on a glass fiber with epoxy. Oscillation and Weissenberg photographs indicated no symmetry; the space group was assigned $P_{\bar{1}}$. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with MoK_α radiation (λ = 0.7107Å) and a graphite monochromator. Lattice parameters were obtained by least-squares refinement of the orientation matrix using 25 centered reflection ($19° < 2\theta < 40°$): a = 9.959(2)Å, b = 12.740(2)Å, c = 15.028(2)Å, α = 94.16(1)°, β = 76.74(1)°, γ = 63.48(1)°, V = 1626.8(5)Å^3.

A total of 20518 intensity measurements were recorded for reflections in the entire sphere ($2\theta \leq 50°$) using ω-2θ scans at a scan speed of 4°/min* with a

* The scan speed for weak reflections was slowed to make $\sigma(I)/I = 0.02$.

Table 1.15. Fractional coordinates (Os(A)–Cl(2D): $\times 10^5$; O–H(46B): $\times 10^4$) and thermal parameters ($U_{eq} \times 10^4$ in Å^2; B in Å^2) for $K_2[\{Os(\eta^4\text{-CHBA-Et})(OPPh_3)\}_2O]\cdot\frac{3}{2}$acetone$\cdot H_2O$.

Label	x	y	z	U_{eq}
Os(A)	21549(7)	5201(8)	20862(5)	330(4)
Os(B)	22403(7)	-3081(8)	32900(5)	342(4)
K(A)	38656(36)	-5101(46)	28668(27)	584(23)
K(B)	92306(41)	-16181(47)	20055(31)	696(25)
P(1A)	21693(42)	7659(52)	9063(35)	457(69)
O(3A)	22183(93)	9606(143)	14329(64)	619(139)
P(1B)	26586(47)	-7880(55)	45206(35)	504(28)
O(3B)	23603(82)	-7434(121)	39547(59)	404(141)
Cl(1A)	41860(61)	46022(62)	27162(42)	1072(39)
Cl(2A)	47787(44)	12102(60)	25529(38)	754(38)
Cl(1B)	34678(49)	-20796(59)	18321(40)	856(36)
Cl(2B)	9253(62)	-39454(58)	15248(44)	1034(42)
Cl(1C)	37223(61)	40764(55)	39150(41)	984(43)
Cl(2C)	47417(47)	8201(61)	38329(37)	817(38)
Cl(1D)	17066(71)	-49684(57)	27331(45)	1164(55)
Cl(2D)	39503(50)	-26485(57)	32344(39)	811(34)

Label	x	y	z	B
O	2181(10)	70(11)	2669(7)	2.80
O(1A)	3240(10)	957(11)	2358(6)	2.95(0.43)
O(1B)	2542(10)	-611(12)	1893(6)	3.72(0.44)
O(2A)	1714(11)	3057(14)	2466(7)	4.71(0.51)
O(2B)	114(11)	-807(12)	1566(7)	4.63(0.50)
N(1A)	1705(12)	1693(14)	2198(8)	3.05(0.54)
N(1B)	1057(13)	134(15)	1780(8)	3.48(0.56)
C(1A)	901(17)	1568(18)	2136(11)	3.71(0.72)
C(2A)	2083(15)	2411(18)	2389(10)	2.40(0.65)
C(3A)	2904(17)	2497(19)	2453(11)	3.44(0.72)
C(4A)	3146(16)	3361(18)	2538(10)	3.04(0.67)
C(5A)	3889(19)	3505(21)	2617(12)	4.92(0.82)
C(6A)	4423(18)	2878(22)	2648(12)	5.08(0.84)
C(7A)	4154(16)	2056(19)	2538(10)	3.41(0.69)
C(8A)	3414(16)	1816(18)	2451(10)	2.85(0.66)
C(1B)	539(17)	917(19)	1705(11)	4.09(0.76)
C(2B)	825(18)	-650(21)	1689(11)	4.25(0.74)
C(3B)	1343(17)	-1406(20)	1714(11)	3.70(0.73)
C(4B)	968(18)	-2205(22)	1619(12)	5.22(0.84)
C(5B)	1430(19)	-2931(21)	1616(12)	4.90(0.82)

Label	x	y	z	B
C(6B)	2169(17)	-2918(19)	1673(11)	3.75(0.72)
C(7B)	2493(17)	-2145(21)	1775(11)	4.02(0.75)
C(8B)	2160(19)	-1314(23)	1780(12)	5.28(0.87)
O(1C)	3249(10)	316(13)	3589(7)	3.82(0.45)
O(1D)	2826(10)	-1392(12)	3182(7)	3.90(0.47)
O(2C)	1423(11)	2093(13)	3616(7)	4.42(0.49)
O(2D)	441(13)	-2020(14)	2723(8)	6.02(0.57)
N(1C)	1663(13)	677(15)	3475(8)	3.86(0.57)
N(1D)	1223(13)	-922(16)	3084(9)	4.08(0.60)
C(1C)	878(18)	420(22)	3429(12)	5.60(0.83)
C(2C)	1852(18)	1528(22)	3567(12)	4.57(0.79)
C(3C)	2683(17)	1746(20)	3659(11)	3.72(0.73)
C(4C)	2797(19)	2646(22)	3725(12)	5.08(0.84)
C(5C)	3529(21)	2889(22)	3829(12)	5.83(0.91)
C(6C)	4128(17)	2405(20)	3847(11)	3.49(0.72)
C(7C)	4020(17)	1521(20)	3788(11)	3.65(0.73)
C(8C)	3293(17)	1158(20)	3676(11)	3.49(0.72)
C(1D)	640(19)	-253(22)	3039(12)	5.63(0.87)
C(2D)	1124(20)	-1743(21)	2905(12)	4.76(0.81)
C(3D)	1748(19)	-2373(21)	2976(11)	4.38(0.79)
C(4D)	1507(18)	-3267(22)	2846(12)	5.19(0.84)
C(5D)	2014(19)	-3918(20)	2870(12)	4.55(0.80)
C(6D)	2741(22)	-3738(24)	2975(14)	6.78(0.98)
C(7D)	3001(18)	-2893(21)	3099(11)	4.36(0.78)
C(8D)	2495(17)	-2188(20)	3059(11)	3.48(0.71)
C(21A)	1695(17)	1692(19)	489(11)	3.70(0.73)
C(22A)	1514(18)	1611(21)	-22(12)	4.66(0.80)
C(23A)	1223(22)	2324(27)	-369(14)	7.27(1.06)
C(24A)	1173(22)	3040(27)	-130(15)	7.97(1.09)
C(25A)	1327(21)	3211(24)	384(14)	6.96(0.99)
C(26A)	1684(19)	2463(23)	755(12)	5.37(0.88)
C(31A)	3081(16)	660(19)	850(12)	4.19(0.73)
C(32A)	3680(23)	455(26)	1255(14)	7.36(1.00)
C(33A)	4381(23)	398(27)	1214(15)	8.20(1.06)
C(34A)	4508(19)	434(22)	774(13)	5.96(0.86)

Label	x	y	z	B
C(35A)	3957(22)	639(24)	350(13)	6.78(0.94)
C(36A)	3215(20)	729(22)	421(13)	6.16(0.92)
C(41A)	1692(17)	-179(19)	678(11)	3.52(0.72)
C(42A)	917(18)	-148(20)	590(11)	4.17(0.77)
C(43A)	493(21)	-919(25)	454(13)	6.75(0.99)
C(44A)	814(21)	-1663(23)	402(13)	6.05(0.91)
C(45A)	1563(21)	-1715(23)	471(13)	6.33(0.95)
C(46A)	2015(19)	-928(24)	611(13)	5.84(0.91)
C(21B)	1931(20)	-782(23)	4739(14)	6.30(0.92)
C(22B)	1995(20)	-561(24)	5249(13)	6.65(0.93)
C(23B)	1296(26)	-800(28)	5436(16)	9.00(1.16)
C(24B)	700(27)	-885(30)	5074(19)	9.90(1.32)
C(25B)	638(29)	-1186(32)	4601(19)	1106(1.44)
C(26B)	1244(24)	-1150(25)	4420(14)	7.29(1.03)
C(31B)	3155(17)	194(20)	4760(11)	4.25(0.77)
C(32B)	3956(20)	162(23)	4998(13)	5.83(0.90)
C(33B)	4322(21)	949(25)	5199(13)	6.60(0.98)
C(34B)	3915(24)	1748(26)	5121(14)	7.76(1.06)
C(35B)	3184(23)	1731(25)	4881(14)	7.12(1.00)
C(36B)	2766(18)	996(23)	4694(12)	5.31(0.86)
C(41B)	3272(17)	-1720(20)	4717(12)	4.09(0.76)
C(42B)	3372(20)	-2109(24)	5198(13)	6.14(0.92)
C(43B)	3852(22)	-2803(25)	5388(14)	7.00(1.02)
C(44B)	4179(22)	-3081(25)	5035(16)	7.51(1.03)
C(45B)	4114(20)	-2787(24)	4571(14)	6.33(0.94)
C(46B)	3645(19)	-2050(22)	4416(12)	5.12(0.84)
A(1A)	5312(16)	-1072(17)	3383(10)	9.08(0.76)
A(2A)	6083(31)	-1177(37)	3582(19)	12.31(1.54)
A(3A)	6147(23)	-2201(28)	3679(15)	9.15(1.19)
A(4A)	6393(27)	-426(34)	3651(17)	12.20(1.44)
A(1B)	8152(32)	-136(37)	948(20)	9.53(1.58)
A(2B)	8257(46)	462(51)	526(27)	9.09(1.80)
A(3B)	8843(32)	679(35)	816(19)	4.26(1.27)
A(4B)	7592(31)	876(34)	791(19)	3.81(1.33)
W	1193(28)	3940(32)	1488(18)	13.28(1.64)

Label	x	y	z	B
H(1A)	846	1334	2449	5.00
H(1A')	647	2134	2066	5.00
H(4A)	2802	3843	2539	5.00
H(6A)	4963	3006	2745	5.00
H(1B)	496	1195	1386	5.00
H(1B')	45	738	1719	5.00
H(4B)	432	-2259	1564	5.00
H(6B)	2447	-3449	1648	5.00
H(1C)	863	169	3745	5.00
H(1C')	558	927	3344	5.00
H(4C)	2392	3067	3693	5.00
H(6C)	4626	2666	3899	5.00
H(1D)	530	37	2712	5.00
H(1D')	179	-528	3065	5.00
H(4D)	971	-3405	2735	5.00
H(6D)	3099	-4208	2967	5.00
H(22A)	1571	1037	-164	5.00
H(23A)	1096	2281	-731	5.00
H(24A)	984	3550	-347	5.00
H(25A)	1217	3783	502	5.00
H(26A)	1876	2521	1116	5.00
H(32A)	3581	324	1570	5.00
H(33A)	4804	335	1518	5.00

Label	x	y	z	B
H(34A)	5013	302	756	5.00
H(35A)	4050	725	28	5.00
H(36A)	2788	842	124	5.00
H(42A)	667	408	622	5.00
H(43A)	-52	-902	392	5.00
H(44A)	507	-2193	311	5.00
H(45A)	1796	-2269	432	5.00
H(46A)	2552	-945	647	5.00
H(22B)	2439	-369	5481	5.00
H(23B)	1302	-436	5771	5.00
H(24B)	232	-887	5164	5.00
H(25B)	163	-1419	4399	5.00
H(26B)	1204	-1362	4084	5.00
H(32B)	4241	-387	5018	5.00
H(33B)	4854	949	5390	5.00
H(34B)	4166	2303	5244	5.00
H(35B)	2919	2288	4834	5.00
H(36B)	2226	1023	4528	5.00
H(42B)	3070	-1883	5399	5.00
H(43B)	3952	-3037	5730	5.00
H(44B)	4508	-3587	5138	5.00
H(45B)	4379	-3064	4360	5.00
H(46B)	3594	-1785	4091	5.00

variable scan width.[§] Background counts were recorded before and after each scan. The integrated intensities were calculated in the following manner: I = R[C − T(B)], where R is the scan rate, C is the scan count, B is the averaged[†] background measurement, and T is the ratio of the scan time to the total background counting time. Three check reflections were remeasured after every 10000 seconds. No decay was observed and no absorption corrections were applied. Transformation of the unit cell resulted in the following lattice parameters: a = 9.959Å, b = 12.173Å, c = 15.079Å, α = 105.28°, β = 76.74°, and γ = 110.53°. Averaging of multiple and symmetry related reflections and deletion of several poorly measured reflections resulted in 9048 unique data; 5690 were greater than 3σ.

Structure determination and refinement. Atomic scattering factors were taken from Stewart, Davidson. and Simpson[55] for H, and the *International Tables for X-ray Crystallography*[56] for all others. The positions of the osmium atoms were derived from a Patterson map, and the subsequent Fourier and difference Fourier maps indicated the locations of all non-hydrogen atoms. Hydrogen atoms, except for those on the hydroxy and methoxy groups and the uncoordinated water molecule, were placed 0.98Å from their respective carbon atom, in idealized positions, and were not refined (B = 4.0). The population of the uncoordinated water molecule was set at 0.25.

Full-matrix least-squares refinement minimized the following function: $\sum w\left(F_o^2 - (F_c/k)^2\right)^2$, $w = \sigma^{-2}(F_o^2)$. Several cycles of least-squares led to the final values for $R = \left\{\sum ||F_o| - |F_c/k||/|F_o|\right\} = 0.100$, $R_{3\sigma}$ (the R-factor calculated using only the reflections with $F_o^2 > 3\sigma(F_o^2)$) = 0.072, and $GOF = \left\{\sum w(F_o^2 - (F_c^2/k))^2/(n_o - n_p)\right\}^{\frac{1}{2}} = 2.14$, where n_o is the number of reflections and n_p is the number of parameters. All atomic coordinates were in one block and the scale factor and the Gaussian ellipsoids were in the other. The final atomic coordinates

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[§] Omega scan angle = 0.8 + 0.35$tan\theta$. Horizontal aperture (mm) = 2.0 + 1.0$tan\theta$.

[†] Averaged for each degree in 2θ.

and Gaussian thermal parameters appear in Table 1.16.

Structure determination of *trans*-$Os(HBA\text{-}TMI)_2Cl_2 \cdot 2DMF$.

Data collection. A crystal, roughly a cube 0.30 mm on a side, was mounted on a glass fiber with epoxy. The intensity data were collected on a locally modified Syntex $P2_1$ automated diffractometer with MoK_α radiation ($\lambda = 0.7107$Å) and a graphite monochromator.

Unit cell parameters were obtained by least-squares refinement of the orientation matrix using 10 centered reflections in the range $13° < 2\theta < 24°$: a = 10.324(23)Å, b = 10.598(12)Å, c = 16.783(17)Å, $\beta = 107.67(13)°$, V = 1750(5)Å^3, Z = 2. The systematic absences led to the assignment of the space group $P2_1/c$ (0k0: k = odd, h0l: l = odd, hkl: none).

A total of 4744 intensity measurements were made in the range ($4.0° < 2\theta < 56.0°$) using θ-2θ scans at a constant scan speed of 4.88°/min and a fixed symmetric scan width of 2° in 2θ. Background measurements were recorded for a time interval equal to half the scan time before and after each scan. The integrated intensities were calculated in the following manner: $I = R[C - T(B_1 + B_2)]$, where R is the scan rate, C is the scan count, B_1 and B_2 are the background measurements, and T is the ratio of the scan time to the total background counting time. Three check reflections were remeasured after every 97 reflections. A decay of 8% was observed; the data were scaled accordingly. Absorption corrections were not applied ($\mu = 40.6$ cm^{-1}). Observational variances, $\sigma^2(F_o^2)$, were based on counting statistics plus a term, 0.02C, where C is the scan count. After deletion of systematic absences, and averaging of multiple and symmetry-related reflections, the total number of unique data was 3448 of which 2041 were greater that 3σ.

Structure determination and refinement. Atomic scattering factors were taken from Stewart, Davidson. and Simpson[55] for H, and the *International Tables for X-ray Crystallography*[56] for all others. The positions of the osmium atoms were derived from a Patterson map, and the subsequent Fourier and difference

Table 1.16. Fractional coordinates (Os–P10: $\times 10^5$; W–HP10: $\times 10^4$) and thermal parameters ($U_{ij} \times 10^4$ in $Å^2$; B in $Å^2$) for *trans*-Os(η^4-CHBA-HMEt)-$(py)_2 \cdot \frac{1}{4}H_2O$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
OS	22623(05)	7817(04)	26342(03)	321(02)	188(02)	310(02)	103(01)	-148(02)	81(01)
CL1	34062(40)	-25322(26)	30523(25)	1008(27)	513(17)	736(23)	468(18)	-517(21)	-11(15)
CL2	56408(33)	22248(28)	47660(24)	506(19)	742(20)	690(23)	39(16)	-347(17)	340(17)
CL3	-7233(61)	-56658(26)	11188(35)	1966(50)	260(16)	1225(38)	111(22)	-1050(38)	18(18)
CL4	76324(42)	64884(27)	37582(30)	782(26)	411(17)	980(31)	-113(17)	-398(24)	67(17)
O1	24461(69)	-7529(49)	27074(44)	379(42)	198(31)	341(39)	94(29)	-179(34)	37(29)
O2	34270(68)	17064(52)	36570(48)	284(39)	273(34)	318(41)	-36(29)	-203(33)	32(29)
O3	-4026(87)	-15471(56)	6966(56)	683(56)	317(37)	573(55)	73(37)	-440(47)	75(34)
O4	28566(108)	42374(67	24252(84)	932(36)	273(36)	1448(93)	36(39)	-842(67)	283(45)
O5	17287(75)	9961(56)	3893(49)	448(39)	408(39)	357(43)	147(34)	-97(36)	167(32)
O6	-4335(74)	18909(59)	25228(55)	372(43)	458(41)	518(50)	259(35)	-75(38)	95(35)
N1	10304(75)	-15(65)	16362(53)	152(39)	353(45)	242(43)	43(34)	-118(34)	85(35)
N2	21179(78)	22609(63)	24081(53)	231(42)	269(41)	287(44)	125(35)	-65(35)	-98(34)
C1	17654(111)	-18232(78)	22754(67)	458(64)	268(48)	236(54)	184(47)	-27(48)	87(40)
C2	20670(129)	-28012(84)	24017(75)	677(79)	299(51)	337(62)	225(53)	-193(59)	43(45)
C3	13100(147)	-39810(88)	20467(92)	901(100)	293(56)	679(89)	293(61)	-371(79)	26(54)
C4	2732(150)	-41973(82)	15172(91)	933(102)	194(48)	601(84)	138(57)	-446(79)	-37(48)
C5	-138(131)	-32772(87)	13037(83)	673(81)	296(54)	494(73)	113(54)	-339(65)	87(49)
C6	7193(102)	-20839(78)	16583(69)	331(56)	259(48)	310(57)	86(43)	-98(47)	78(41)
C7	4247(105)	-11706(80)	13096(70)	328(58)	313(51)	334(58)	113(45)	-136(48)	57(42)
C8	7513(103)	8405(73)	12044(73)	320(56)	253(45)	398(63)	96(41)	-192(50)	48(41)
C9	9120(102)	20287(78)	19142(72)	302(56)	303(50)	386(63)	104(43)	-145(49)	143(45)
C10	29927(109)	33927(83)	26350(83)	342(60)	277(52)	598(78)	73(46)	-172(56)	155(49)
C11	41970(111)	36186(81)	31699(78)	361(61)	286(51)	449(70)	94(46)	-173(54)	28(46)
C12	52450(127)	47587(83)	32308(87)	562(77)	242(50)	564(79)	81(51)	-222(65)	70(49)
C13	63500(116)	50740(89)	37131(86)	325(64)	323(58)	589(81)	-31(49)	-120(59)	42(53)
C14	64687(115)	43282(98)	42089(89)	291(62)	523(70)	566(82)	52(54)	-138*58)	51(59)
C15	54642(110)	32056(82)	41674(76)	359(60)	330(53)	417(66)	62(45)	-245(53)	3(45)
C16	43090(99)	27930(80)	36632(67)	196(50)	333(52)	282(54)	61(42)	-58(42)	36(41)
CME	-5979(162)	29626(117)	30962(106)	890(107)	656(88)	673(99)	532(83)	105(84)	26(72)
PN1	4139(83)	5925(57)	36274(55)	368(49)	165(34)	333(48)	102(33)	-148(40)	79(32)
P1	3687(119)	133997(100)	44104(78)	377(65)	613(72)	317(62)	133(56)	-76(53)	25(53)
P2	-8023(146)	13859(108)	50712(92)	629(88)	653(82)	448(79)	161(70)	-154(72)	15(62)
P3	-20704(124)	4266(100)	49797(85)	478(74)	584(74)	451(76)	259(62)	38(62)	238(61)
P4	-20682(123)	-4302(96)	42047(89)	394(69)	443(66)	554(80)	49(55)	5(62)	147(57)
P5	-8192(127)	-3087(93)	35551(79)	540(76)	456(64)	363(66)	179(58)	-13(59)	72(51)
PN2	42551(83)	9954(57)	17644(55)	349(47)	171(35)	326(46)	103(33)	-133(39)	54(31)
P6	46600(114)	14903(95)	10083(83)	327(61)	518(66)	423(71)	151(52)	-23(55)	120(54)
P7	60223(133)	16680(104)	5062(89)	499(78)	652(79)	478(80)	218(65)	116(64)	264(63)
P8	70330(140)	13331(110)	7752(104)	467(81)	594(80)	698(101)	265(67)	108(73)	67(70)
P9	66212(136)	8290(119)	15269(99)	499(83)	865(94)	597(91)	382(74)	-95(72)	236(73)
P10	52980(108)	6670(104)	19807(86)	274(56)	753(82)	529(79)	334(57)	-15(53)	203(63)

Atom	x	y	z	B
W	3624(44)	5204(33)	9846(31)	6.3(0.9)
H3	1525	-4642	2179	4.0
H5	-740	-3457	898	4.0
H8	-277	529	1038	4.0
H9	1131	2712	1620	4.0
H12	5167	5333	2912	4.0
H14	7247	4586	4586	4.0
HP1	1258	2062	4520	4.0
HP2	-765	2045	5614	4.0
HP3	-2929	377	5460	4.0
HP4	-2930	-1126	4102	4.0
HP5	-842	-938	2993	4.0
HP6	3955	1731	808	4.0
HP7	6276	2035	-43	4.0
HP8	6040	1458	430	4.0
HP9	7304	580	1742	4.0
HP10	5035	277	2517	4.0

Fourier maps indicated the locations of the remaining non-hydrogen atoms; the hydrogen atoms were placed at calculated positions 0.98Å from their respective carbon atom and were not refined.

Full-matrix least-squares refinement minimized the following function: $\sum w\left(F_o^2 - (F_c/k)^2\right)^2$, $w = \sigma^{-2}(F_o^2)$. Twenty percent of the data from the inner shell ($2\theta < 32°$), based on the number of unique data,were then excluded due to crystal absorption. Subsequent cycles of least squares using the remaining 2692 reflections (1411 greater than 3σ) led to the final values for $R = \left\{ \sum ||F_o| - |F_c/k|| / |F_o| \right\} = 0.111$, $R_{3\sigma}$ (the R-factor calculated using only the reflections with $F_o^2 > 3\sigma(F_o^2)$) $= 0.056$, and $GOF = \left\{ \sum w\left(F_o^2 - (F_c^2/k)\right)^2 / (n_o - n_p) \right\}^{\frac{1}{2}} = 1.36$, where n_o is the number of reflections and n_p is the number of parameters. All atomic coordinates were in one block and the scale factor and the Gaussian ellipsoids were in the other. The final model with all the data gave $R = 0.095$, $R_{3\sigma} = 0.065$, and $GOF = 3.49$. The final atomic coordinates and Gaussian thermal parameters appear in Table 1.17.

Table 1.17. Fractional coordinates (Os–SO1: $\times 10^5$; H1–H16: $\times 10^4$) and thermal parameters ($U_{eq} \times 10^4$ in Å^2; B in Å^2) for *trans*-Os(η^2-(H)HBA-TMI)$_2$-Cl_2·2DMF.

	x	y	z	U_{eq}
Os	0(0)	0(0)	0(0)	282(1)
Cl	−8772(36)	9827(27)	−13043(16)	410(4)
O1	18854(82)	347(174)	−858(58)	445(12)
N1	4040(103)	17891(84)	5643(50)	321(12)
N2	13139(114)	36724(87)	7991(64)	353(14)
C1	25277(125)	10494(92)	−2452(71)	344(16)
C2	35945(133)	8622(139)	−5987(98)	446(21)
C3	43525(163)	18152(152)	−7481(116)	503(24)
C4	40846(177)	30748(145)	−5723(100)	487(23)
C5	30883(158)	32605(124)	−1834(84)	427(19)
C6	22775(125)	22907(98)	−176(65)	333(15)
C7	12957(130)	25411(92)	4353(61)	333(15)
C8	5434(142)	36175(119)	13835(70)	395(18)
C9	−1667(152)	48449(117)	14481(91)	508(23)
C10	15310(212)	32716(205)	22623(98)	572(30)
C11	−4450(115)	24845(99)	9856(66)	329(14)
C12	−8410(182)	17055(151)	16444(86)	487(22)
C13	−17524(153)	29720(145)	2982(107)	480(24)
SC1	56305(435)	26824(246)	18848(214)	823(56)
SC2	43253(278)	7394(244)	20067(195)	834(50)
SN1	55277(200)	15685(165)	23607(92)	572(27)
SC3	64237(152)	13087(153)	30667(125)	535(25)
SO1	63601(214)	3618(127)	35065(115)	696(28)

	X	Y	Z
H1	3716	−48	−756
H2	5108	1574	−987
H3	4631	3777	−670
H4	2920	4157	−8
HN	1839	4435	736
H5	483	5457	1775
H6	−562	5175	869
H7	−918	4739	1693
H8	1139	2544	2527
H9	1747	3946	2640
H10	2375	2897	2177
H11	−1876	1502	1453
H12	−396	868	1729
H13	−672	2117	2190
H14	−1523	3692	9
H15	−2126	2288	−104
H16	−2476	3231	549

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Chapter 2
A Survey of the Organometallic Chemistry of Osmium Tetraoxide.

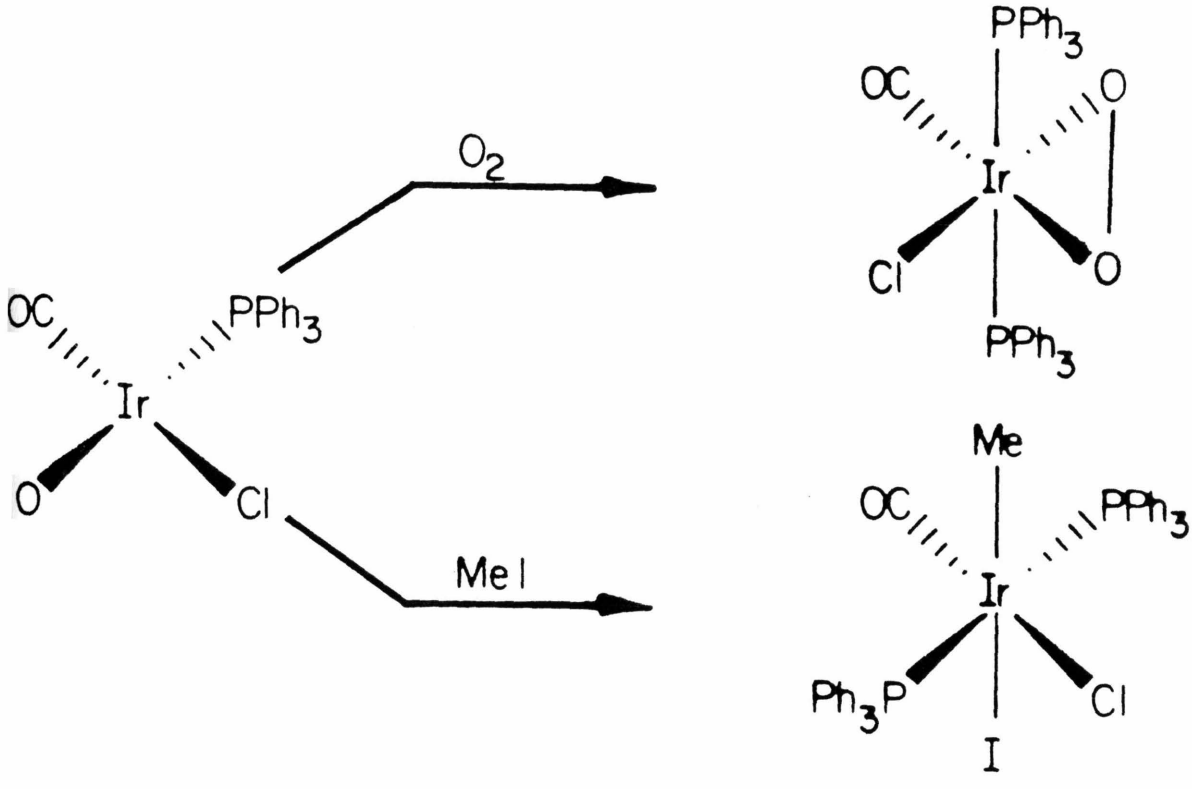
Introduction

The chemistry of oxidants and inorganic/organometallic compounds has continued to be an area of active interest for the past several decades.[1] The emergence of organometallic chemistry in the late 1950's and 1960's has led to the characterization of oxidative addition reactions, *e.g.*, the reaction of methyl iodide or molecular oxygen with *trans*-$IrCl(CO)(PPh_3)_2$[2,3] (Figure 2.1). Studies of metal-based inner- and outer-sphere electron transfer processes have grown in importance stemming from their applicability as model systems of biological and biochemical phenomena.[4] Currently, advances in both oxidation chemistry and inorganic/organometallic chemistry have facilitated studies on the reactivity of classical oxidants, *e.g.*, iodosylbenzene, organic peracids, and osmium tetraoxide, with low valent transition metal complexes.[5] The goals of these investigations are to better understand the reactions available to this class of oxidants and to ultimately develop selective oxidation reactions for organometallic synthesis.

Iodosylbenzene has recently been shown to perform several fundamental oxygen transfer reactions. The utility of this reagent as an oxidant of organic substrates via transition metal complexes has been demonstrated.[6] In many instances, the oxidized transition metal complex is the active reagent for the oxidative transformation of the organic species. Groves[7] has characterized several reactive high valent chromium-oxo-porphyrinato compounds derived from iodosylbenzene oxidation of lower valent species. The oxidation of coordinated ligands by oxygen atom transfer reactions has a number of precedents. For instance, Gladysz has produced the rare formaldehyde ligand[8] in the compound, $[CpRe(\eta^2\text{-}CH_2O)(NO)(PPh_3)]PF_6$, by treating the cationic methylidine complex, $[CpRe(=CH_2)(NO)(PPh_3)]PF_6$, with iodosylbenzene in dichloromethane ($-23°C$).[9]

There are many reagents such as iodosylbenzene where the fundamental reaction chemistry with inorganic/organometallic complexes remains to be investigated. Studies of the fundamental reactions of metal-oxo compounds with low valent organometallic complexes are very rare. There is, however, an obvi-

Figure 2.1. Oxidative addition reactions of methyl iodide and molecular oxygen with Vaska's complex, *trans*-$IrCl(CO)(PPh_3)_2$.


OC
PPh3
Ir
O
Cl
O2
MeI
PPh3
OC
O
Ir
Cl
O
PPh3
Me
OC
PPh3
Ir
Ph3P
Cl
I

ous conceptual connection, since it is clear that reactions between the two types of molecules will occur. Oxidations by osmium tetraoxide have been examined by our group. One can conceive of several possible modes of reactivity for this reagent with low valent organometallic complexes by drawing analogies with the osmium tetraoxide oxidations of alkenes, which have been studied in some detail.

Oxidation of 2,3-dimethylbut-2-ene with osmium tetraoxide results in the formation of dimeric monoester complexes,† *syn*- and *anti*-$Os_2O_4(O_4C_6H_{12})_2$ (Figure 2.2a,b); the *anti* form has been isolated and structurally characterized.[10] In the presence of nitrogenous bases, *e.g.*, pyridine, monomeric diolatodioxobis(amine)osmium(VI) ester complexes (Figure 2.2c) are formed.[10] The infrared spectrum for this monomeric compound shows strong bands near 840 cm^{-1} assigned to the asymmetric stretching vibration, $\nu^{as}(OsO_2)$; the dimeric complexes exhibit strong bands near 980 cm^{-1} assigned to the $Os{=}O_{terminal}$ stretching mode.

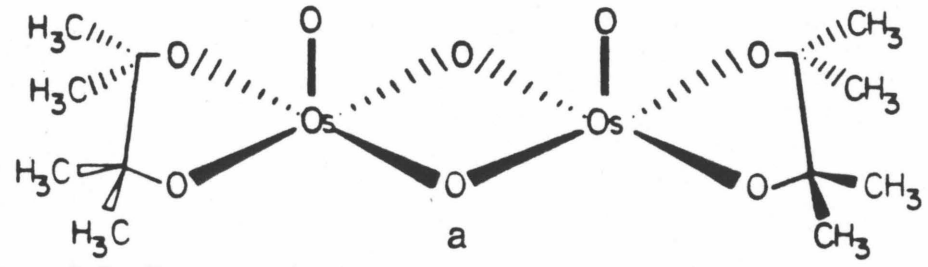
Until recently, the mechanism of alkene oxidation was thought to involve direct oxygen attack at the carbon-carbon double bond via the familiar six-π-electron cyclic transition state[11] (Figure 2.3a). Sharpless[12] in 1977 proposed an alternative mechanism in which the alkene attacks the electron-impoverished osmium center,‡ to form, via an η^2-alkene complex, an asymmetric four-membered cyclic intermediate (Figure 2.3b); the intermediate subsequently rearranges to the observed five-membered cyclic ester. The experimental data can be rationalized for either mechanism; the "Sharpless intermediate" has not, as yet, been observed.[13]

Based on these organic oxidations, plausible reaction pathways for inorganic/-organometallic systems range from a simple dative interaction (*cf.* the first stage of the Sharpless mechanism) to a formal oxidative addition of the osmium tetraoxide (Figure 2.4a,b,c). Oxidation of two molecules by one electron or oxidation

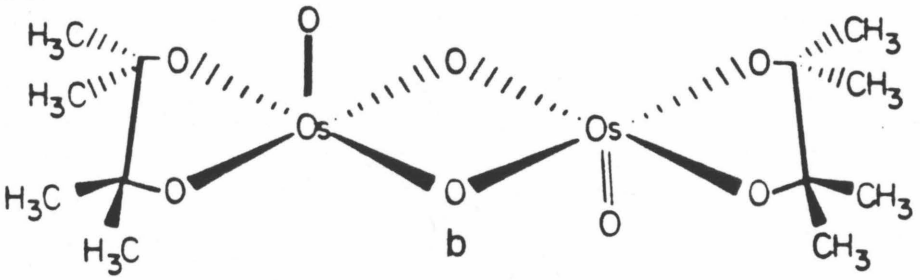
† Secondary substitution reactions result in the formation of diester and trinuclear osmium complexes.

‡ This reaction is similar to nucleophilic attack of organic carbonyls.

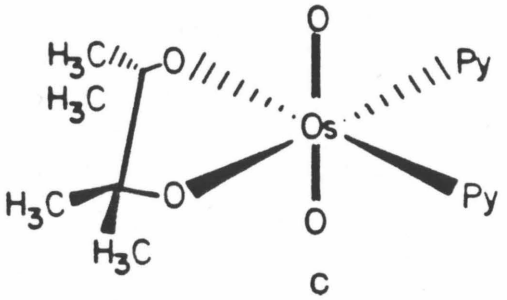
Figure 2.2. Structures of characterized osmium(VI)-oxalato complexes.


H3C
H3C
H3C
H3C
O
O
O
O
O
O
O
O
Os
Os
CH3
CH3
CH3
CH3

a


H3C
H3C
H3C
H3C
O
O
O
O
O
O
O
O
Os
Os
CH3
CH3
CH3
CH3

b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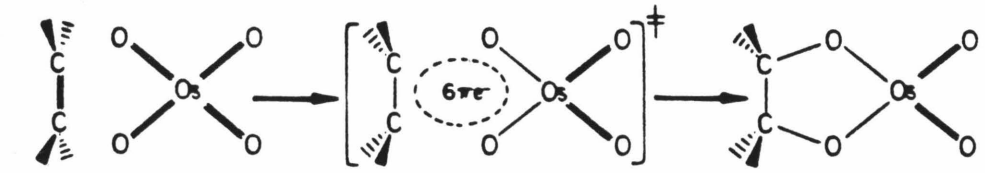
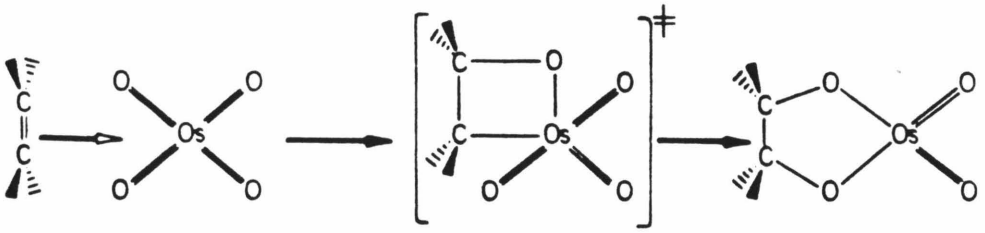
H3C
H3C
H3C
O
O
O
O
O
Os
Py
Py

c

Figure 2.3. Proposed mechanisms for the oxidation of alkenes by osmium tetraoxide.



a



b

of dimeric compounds may produce trinuclear complexes with the O–$Os(O)_2$–O moiety bridging the two metal centers (Figure 2.4d,e). Oxidation of coordinated ligands may also be possible.

The reactivity of osmium tetraoxide with *trans*-$IrCl(CO)(PPh_3)_2$ has recently been investigated;[14] the results were not totally as expected. In the presence of *t*-butylpyridine attack of *both* the iridium center and the coordinated carbonyl ligand was observed. The dinuclear complex, formed in this reaction, contains what is formally a μ-carbon dioxide moiety bridging the iridium and osmium centers. An *X*-ray crystallographic structure determination was undertaken on a derivative of this product, *viz.* $[(PPh_3)_2(4\text{-}t\text{-Bupy})(t\text{-BuNC})Ir(\mu\text{-O})(\mu\text{-C}(OCH_3)O)OsO_2(4\text{-}t\text{-Bupy})_2](ClO_4)_2$ (Figure 2.5), to support this unusual result, which was unambiguously characterized by spectroscopic methods.

This is the first well characterized example of bridging η^2-CO_2 coordination. Other modes of carbon dioxide coordination are known. Herskovitz[15] has examined a series of rhodium and iridium complexes which exhibit an unprecedented η^1-M-CO_2 structure, *e.g.*, $Rh(diars)_2Cl(CO_2)$ (Figure 2.6a). Lappert[16] and Aresta[17] have characterized η^2-CO_2 complexes in which the carbon and oxygen atoms are coordinated to the same metal (Figure 2.6b,c). Coordination to all three atoms has also been discovered. Floriani[18] has reported the synthesis of a polymeric cobalt complex in which the potassium counterion interacts strongly with both oxygen atoms (Figure 2.6d). Several osmium-carbonyl clusters also bind carbon dioxide;[19] the η^3-CO_2 bridges two cluster units (Figure 2.6e). Beck[20] has characterized an unusual μ^3-CO_2 bridged dimer, $\{(CO)_5Re(\mu^3\text{-}CO_2)Re(CO)_4\}_2$ (Figure 2.6f).

The η^2-CO_2 structure, bridging two metal centers, has been proposed previously. Floriani[21] treated $\{CpTiCl\}_2$ with CO_2 (10 atm, 90°C) and recovered $\{CpTiCl\}_2O$ and CO (≈90%); the suggested reactive intermediate was the μ-CO_2 complex, $CpClTi(\mu\text{-}CO_2)TiClCp$. A preliminary communication on a rhodium complex,[22] $(PPh_3)_3Rh_2(CO)_2(CO_2)_2$, reported three bands attributable to the coordinated CO_2 ligands (1600(s), 1355(s), 825(w) cm^{-1}); *cf.* the spectrum of

Figure 2.4. Plausible reaction pathways for the interaction of osmium tetraoxide with low valent organometallic complexes.

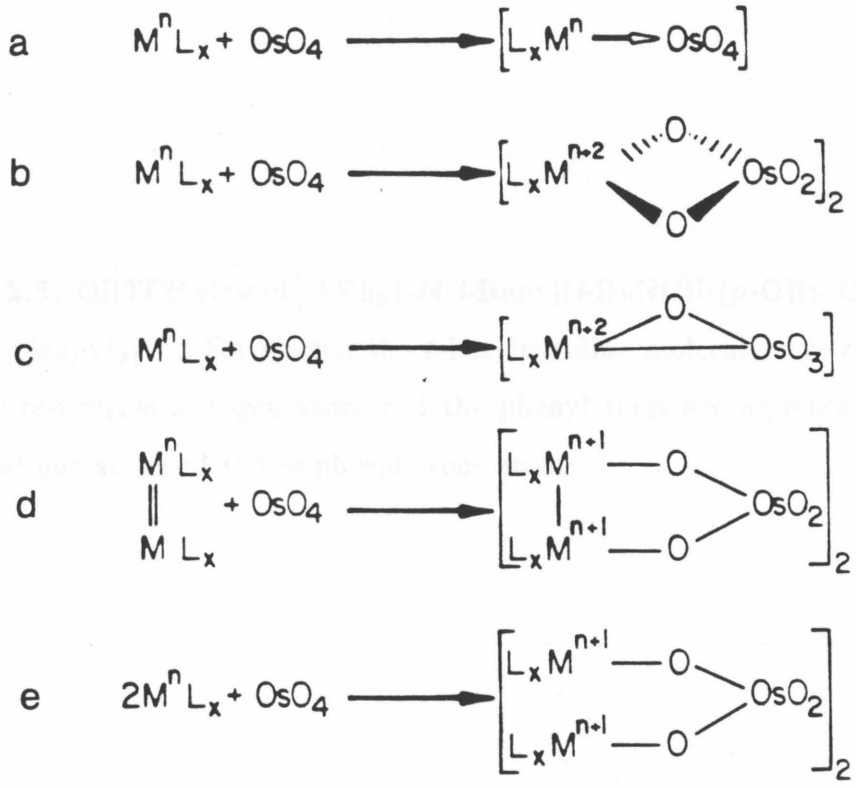

a
$M^nL_x + OsO_4 \longrightarrow [L_xM^n \rightarrow OsO_4]$
b
$M^nL_x + OsO_4 \longrightarrow [L_xM^{n+2}(O)(O)OsO_2]_2$
c
$M^nL_x + OsO_4 \longrightarrow [L_xM^{n+2}(O)OsO_3]$
d
$M^nL_x \| ML_x + OsO_4 \longrightarrow [L_xM^{n+1}(-O-)(|)L_xM^{n+1}(-O-)OsO_2]_2$
e
$2M^nL_x + OsO_4 \longrightarrow [L_xM^{n+1}(-O-)L_xM^{n+1}(-O-)OsO_2]_2$

Figure 2.5. ORTEP view of $[(PPh_3)_2(4\text{-}t\text{-Bupy})(t\text{-BuNC})Ir(\mu\text{-O})(\mu\text{-C(OCH}_3)O)\text{-}OsO_2(4\text{-}t\text{-Bupy})_2]^{+2}$. For clarity, the *t*-butylpyridine molecules are represented by their respective nitrogen atom and the phenyl rings are represented by the carbon atoms attached to the phosphorous atoms.

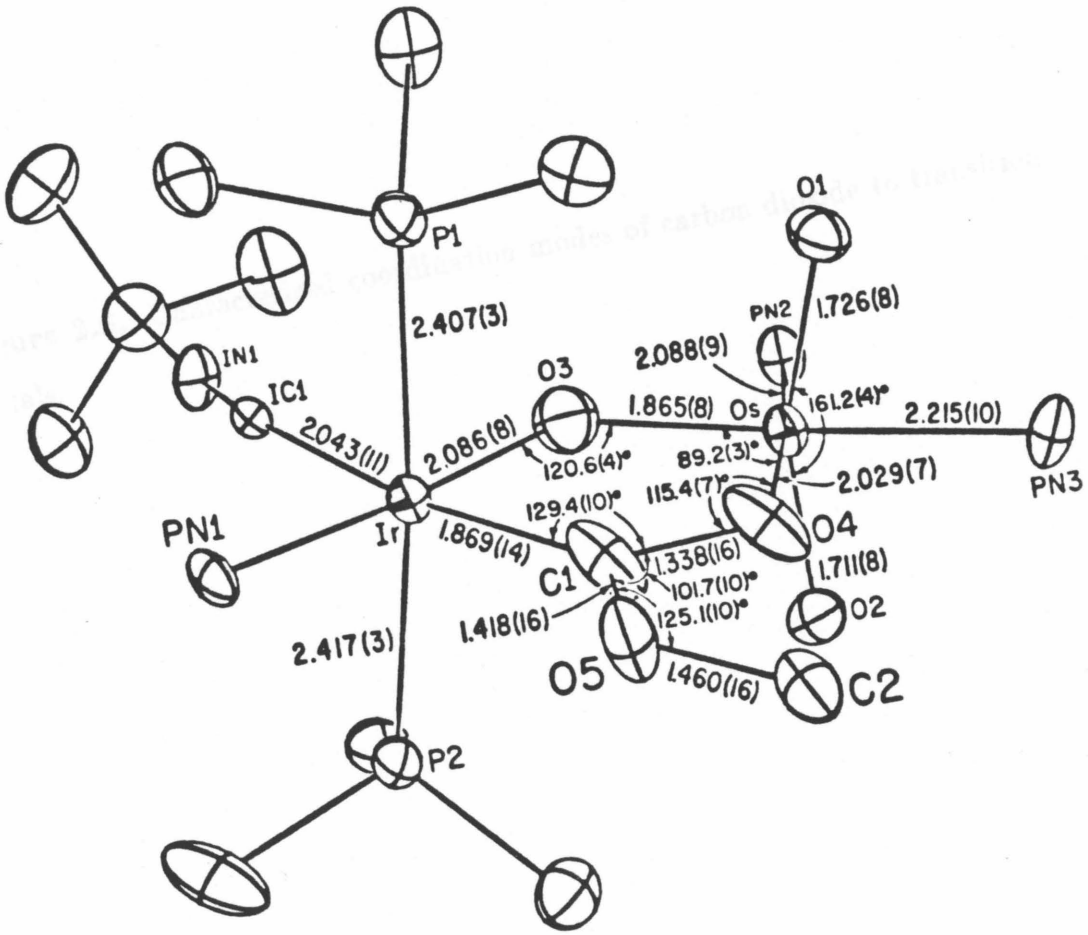
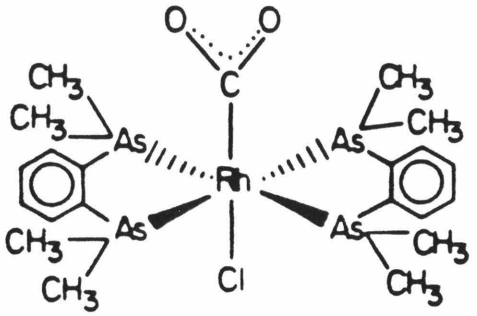
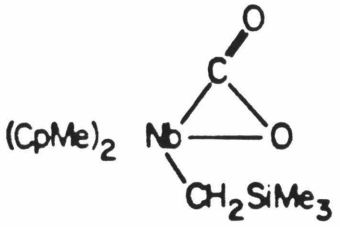

P1
2.407(3)
IN1
IC1
2.043(11)
2.086(8)
O3
1.865(8)
Os
2.088(9)
PN2
1.726(8)
O1
161.2(4)°
2.215(10)
PN3
89.2(3)°
120.6(4)°
115.4(7)°
2.029(7)
O4
PN1
Ir
1.869(14)
129.4(10)°
C1
1.338(16)
101.7(10)°
125.1(10)°
1.711(8)
O2
1.418(16)
O5
1.460(16)
C2
2.417(3)
P2

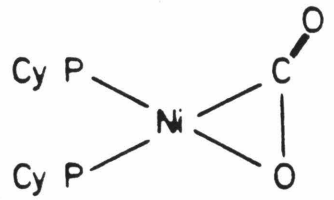
Figure 2.6. Characterized coordination modes of carbon dioxide to transition metals.


O
O
C
CH3
CH3
As
Rh
As
CH3
CH3
As
As
CH3
CH3
CH3
Cl
CH3

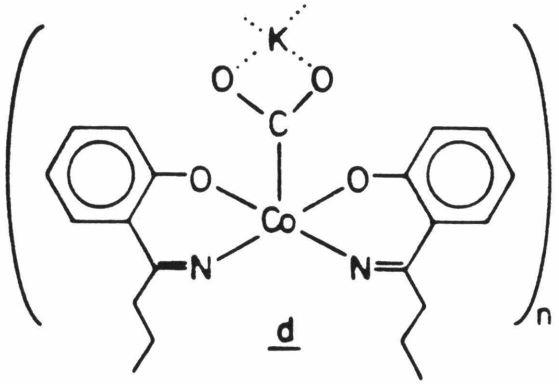
a


O
C
(CpMe)2
Nb
O
CH2SiMe3

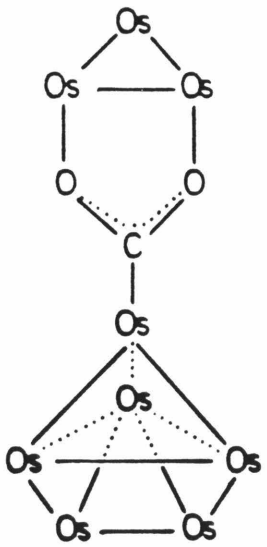
b


O
Cy P
C
Ni
Cy P
O

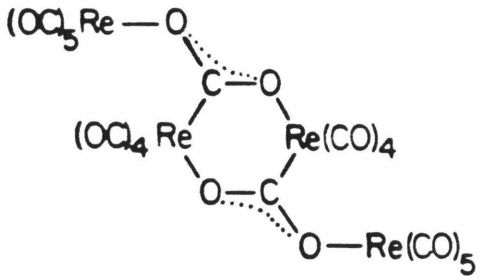
c


K
O
O
C
O
O
Co
N
N
n

d


Os
Os
Os
O
O
C
Os
Os
Os
Os
Os
Os

e


(OC)5Re
O
C
O
(OC)4 Re
Re(CO)4
O
C
O
O
Re(CO)5

f

$(PPh_3)_2Cl(4\text{-}t\text{-}Bupy)Ir(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(4\text{-}t\text{-}Bupy)_2$ (1593(s), 1022(s) cm^{-1}). The CO_2 bonding mode is not known. Bridging μ-CO_2 coordination is a possible structure for this molecule. An interesting alternative is a structure in which the two carbon dioxide molecules dimerize in a head-to-tail fashion, as was found for $IrCl(C_2O_4)(PMe_3)_3$[23] (Figure 2.7); the infrared spectrum for this compound, however, exhibits many more bands (1725(s), 1680(s), 1648(s), 1605(s), 1290(s), 1005(m), and 790(m) cm^{-1}).

Another mode of reactivity was also found. The reaction of osmium tetraoxide and *trans*-$IrCl(CO)(PPh_3)_2$ in the absence of nitrogenous bases[14] resulted in the formation of a partially characterized complex in which the coordinated carbonyl ligand was not oxidized. Based on infrared data and the stoichiometry of the reaction, two structures have been proposed as shown in Figure 2.8; the second structure is thought more reasonable. Few other details are known.

The initial work on the organometallic chemistry of osmium tetraoxide inspired the investigation presented below. Several unanswered questions invited additional study: Could other organometallic substrates be cleanly oxidized by osmium tetraoxide? Was attack at the coordinated carbonyl ligand a general reaction? Could it be extended to nitrosyl, thiocarbonyl, and isocyanide complexes? Were there other modes of reactivity available to osmium tetraoxide? An *X*-ray structural study of an authentic μ-CO_2 complex was also warranted.

Figure 2.7. Structure of $IrCl(C_2O_4)(PMe_3)_3$.

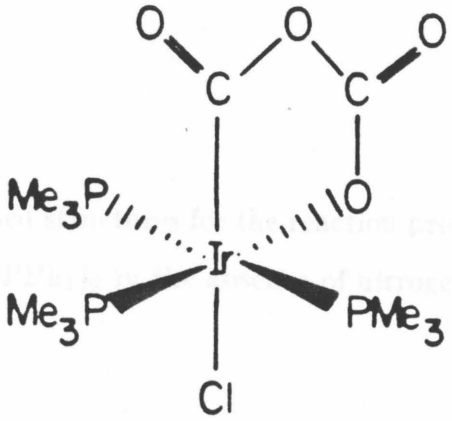
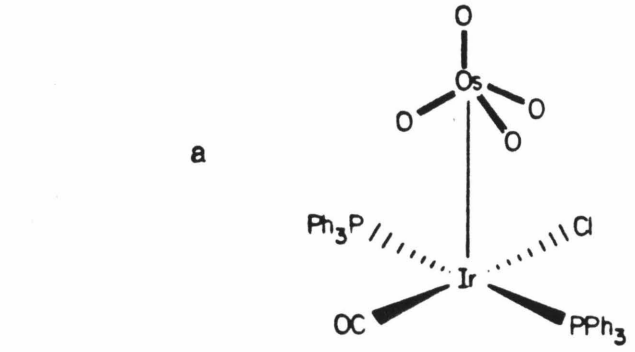
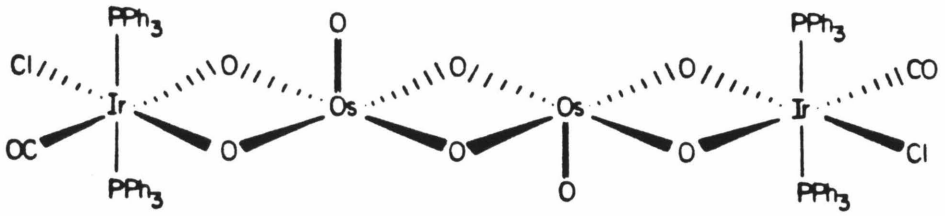

O
O
O
C
C
O
Me3P
Ir
Me3P
PMe3
Cl

Figure 2.8. Proposed structures for the reaction products of osmium tetraoxide and *trans*-$IrCl(CO)(PPh_3)_2$ in the absence of nitrogenous bases.

a


O
Os
O
O
O
Ph3P
Cl
Ir
OC
PPh3


PPh3
Cl
Ir
OC
PPh3
O
O
O
Os
O
O
O
Os
O
O
O
PPh3
Ir
CO
Cl
PPh3

b

Results and Discussion

Several low valent organometallic complexes have been examined. Treatment of $Ru(CO)_3(PPh_3)_2$ or $Os(CO)_3(PPh_3)_2$ with the stable quinuclidine adduct of osmium tetraoxide afforded yellow complexes containing the bridging carbon dioxide moiety (Figure 2.9). This formulation was supported by the appearance of strong infrared bands attributable to C=O and symmetric and asymmetric C≡O stretching modes. Interestingly, the positions of these bands were dependent on the method of isolation. The dinuclear products precipitated spontaneously on mixing the reactants in benzene (Ru: ν(C≡O) at 2025, 1973 cm^{-1}, ν(C=O) at 1551 cm^{-1}; Os: ν(C≡O) at 2015, 1952 cm^{-1}, ν(C=O) at 1550 cm^{-1}) or it was isolated from dichloromethane by addition of hexanes (Ru: ν(C≡O) at 2009, 1973 cm^{-1}, ν(C=O) at 1602 cm^{-1}; Os: ν(C≡O) at 2000, 1934 cm^{-1}, ν(C=O) at 1550 cm^{-1}). Note that there is a 50 cm^{-1} solvent-dependent difference in ν(C=O). Both forms were analytically pure and could be interconverted. Solid-state ^{31}P NMR spectra of the two ruthenium compounds (Figure 2.10), were found to be different, yet consistent with *trans* phosphines;[†] solution ^{31}P NMR spectrum (CD_2Cl_2) of the analogous osmium complex exhibited one singlet ($\delta = -0.74$).[‡]

The structural differences between the two forms is most likely due to solid state effects. The subtle changes are not known. A discrete dinuclear complex (ν(CO) at 1602 cm^{-1}) and a weakly bound dimer/polymer (Figure 2.11b) in which the carbonyl oxygen coordinates weakly to the five-coordinate osmium center (ν(CO) at 1550 cm^{-1}) is a possible assignment. However, the infrared bands for Beck's μ^3-CO_2 complex[20] (Figure 2.6f) are much lower ($\nu(CO_2)$: 1380, 1295, 1260 cm^{-1}).

The stability of these complexes is thought to be kinetically rather than thermodynamically controlled. Free carbon dioxide has been found to coordinate

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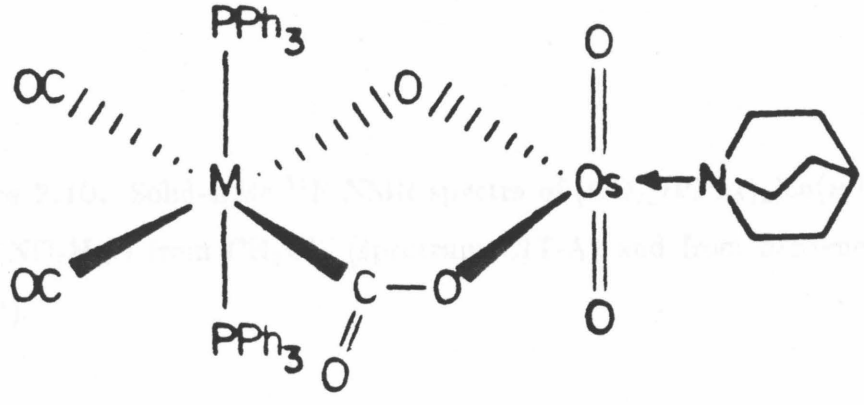
[†] Some broadening was observed, but this is not uncommon with solid-state ^{31}P NMR spectra.[24]

[‡] The scale (δ) is relative to external H_3PO_4.

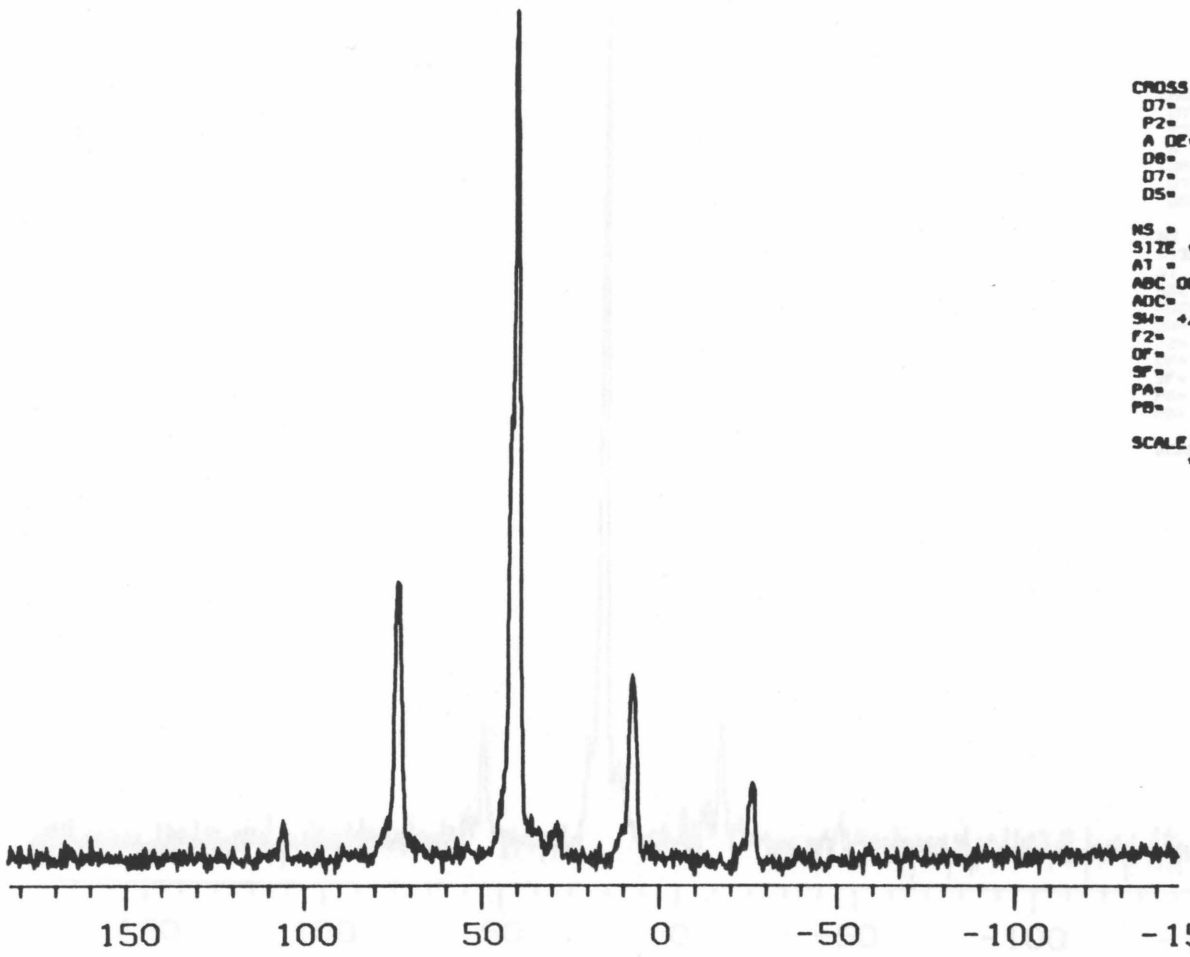
Figure 2.9. Proposed structures for the reaction products of $OsO_4(NC_7H_{13})$ with $Ru(CO)_3(PPh_3)_2$ and $Os(CO)_3(PPh_3)_2$.



M = Ru, Os

Figure 2.10. Solid-state ^{31}P NMR spectra of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)\text{-}OsO_2(NC_7H_{13})$ from CH_2Cl_2 (spectrum CIT-A) and from benzene (spectrum CIT-B).

COL908. 000 FRYE 08SEP83
P-31 CPMAS JF: CIT-A



cSu

COLORADO STATE UNIVERSITY
REGIONAL NMR FACILITY

303-491-6455

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P2= 9.00 MSEC
A DE= 50 USEC
D8= 52.00 MSEC
D7= 7.00 USEC
D5= 1.00 SEC

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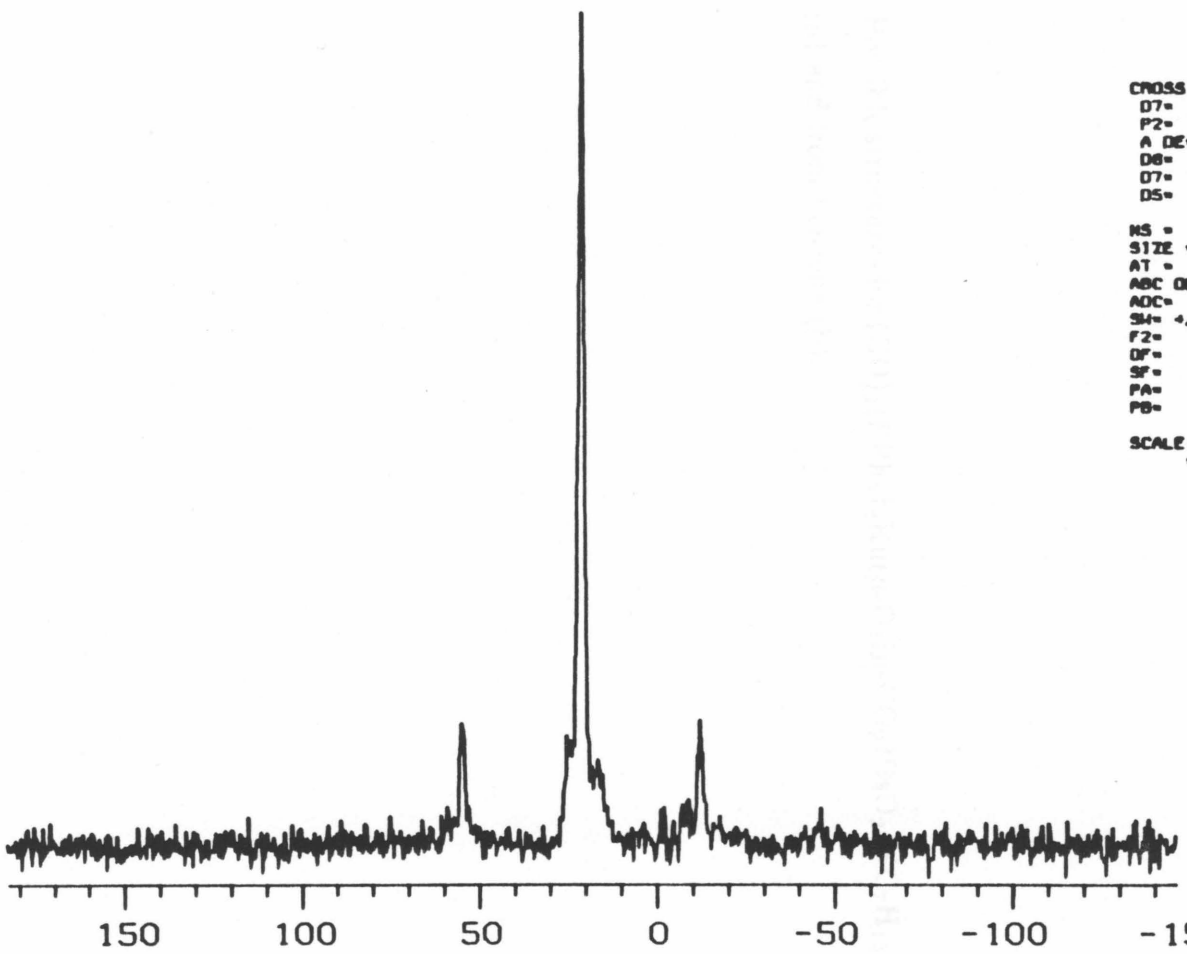
SIZE = 2048
AT = 102.45 MSEC
ABC ON OPD ON = 1
ADC= 12 BITS A1= 9
SW= +/- 10000.0 DW= 50
F2= 150.000000
OF= 1119.89
SF= 80.745000
PA= 81.4
PB= 428.5

SCALE: 1000.00 HZ/CM
= 18.4822 PPM/CM

COL908. 100 FRYE 08SEP83
P-31 CPMAS JF: CIT-B



CSU

COLORADO STATE UNIVERSITY
REGIONAL NMR FACILITY

303-491-6155

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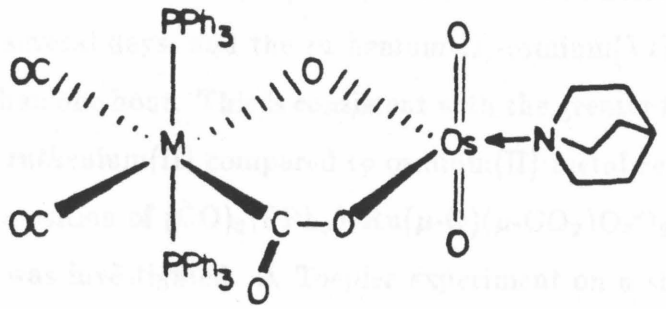
P2= 9.00 MSEC
A DE= 50 USEC
D8= 52.00 MSEC
D7= 7.00 USEC
D5= 1.00 SEC

NS = 224
SIZE = 2048
AT = 102.45 MSEC
ADC ON OPD ON = 1
ADC= 12 BITS A1= 9
SW= +/- 10000.0 DW= 50
F2= 150.000000
OF= 1119.88
SF= 80.745000
PA= 100.5
PB= 971.7

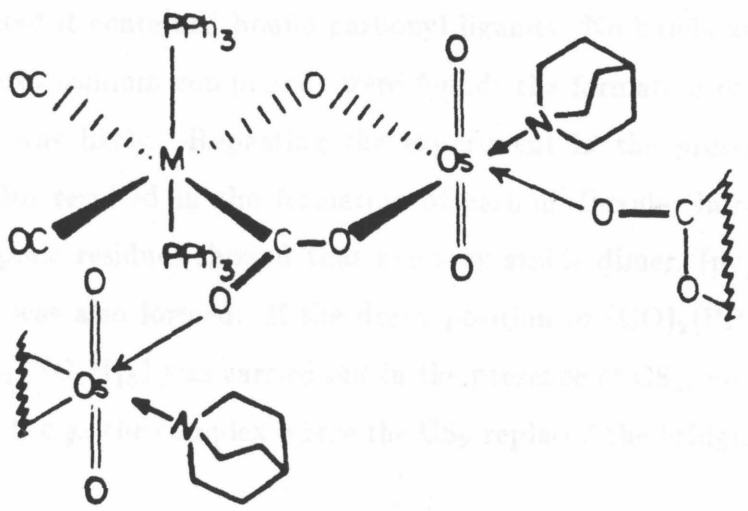
SCALE: 1000.00 HZ/CM
= 18.4822 PPM/CM

Figure 2.11. Possible structures for $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ from CH_2Cl_2 (a) and from benzene (b).

a


PPh3
OC
O
M
Os
N
OC
C
O
O
PPh3
O
O

b


PPh3
OC
O
M
Os
O
N
OC
C
O
O
PPh3
O
O
Os
N
O
O

M = Ru, Os

only to electron-rich metal centers (*vide supra*). However, osmium tetraoxide oxidation of the carbonyl ligand in essence traps the CO_2 moiety between the oxidized organometallic center and the osmium(VI) center. Decomposition of this complex therefore depends on the lability of this μ-CO_2 group. The iridium(III)-osmium(VI) complex, $(PPh_3)_2(t\text{-Bupy})ClIr(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(t\text{-Bupy})_2$, studied by Audett and Collins,[14] was found to be stable in solution, which is in keeping with the propensity of iridium(III) complexes to be very inert to substitution. The osmium(II)-osmium(VI) complexes, described here, were only stable in solution for several days, and the ruthenium(II)-osmium(VI) complexes were stable for less than one hour. This is consistent with the greater lability of ligands coordinated to ruthenium(II) compared to osmium(II) metal centers.

The decomposition of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ in dichloromethane was investigated. A Toepler experiment on a sample stirred for 24 hours under vacuum recovered approximately 1 equivalent of CO_2; the dark-brown inorganic material was not fully characterized. Infrared spectroscopic evidence indicated it contained bound carbonyl ligands. No bands attributable to mono- or dioxo osmium compounds were found; the formation of polymeric osmium oxides was likely. Repeating the experiment in the presence of excess pyridine also resulted in the formation of carbon dioxide; infrared spectra of the inorganic residues showed that the very stable dimer, $(py)_2OsO_2(\mu\text{-}O)_2OsO_2(py)_2$, was also formed. If the decomposition of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ was carried out in the presence of CS_2, no new products were formed, *e.g.*, the complex where the CS_2 replaced the bridging η^2-CO_2 moiety.

An unusual tetranuclear complex (Figure 2.12) was obtained on mixing solutions of osmium tetraoxide and $Ru(CO)_3(PPh_3)_2$ (each in benzene). Attack at the ruthenium center and the coordinated carbonyl ligand was observed. Strong carbonyl bands appeared in the infrared spectrum at 2020, 1988 and 1622 cm^{-1}. The ν(OsO) band was found at 972 cm^{-1}, which is typical of five-coordinate dimeric mono-oxo osmium(VI) complexes (see Figure 2.2a,b). Elemental analysis

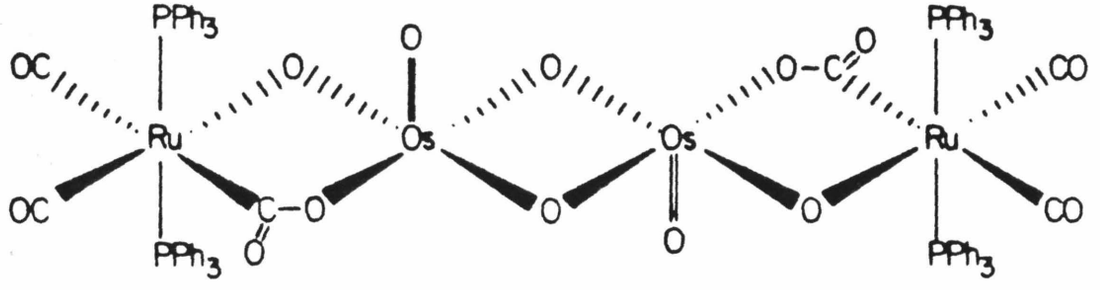
and ^{1}H NMR also support this formulation. Unfortunately, the poor solubility of this complex hindered attempts to determine the molecular weight. No tractable complexes were formed in the presence of pyridine — a distinct contrast to earlier work.[14]

Treatment of $Ru(NO)Cl(CO)(PPh_3)_2$ or $Pt(CO)(PPh_3)_2$ with the quinuclidine adduct of osmium tetraoxide also resulted in attack at the metal center and the coordinated carbonyl ligand. Decomposition of the complexes hindered the isolation of analytically pure samples. The nitrosyl ligand in $Ru(NO)Cl(CO)(PPh_3)_2$ was found to be oxidatively sensitive (*vide infra*). Free carbon dioxide (0.48 equiv.) was collected from a solution of crude $(PPh_3)_2Pt(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ after 24 hours.

Little is known about the mechanism of these unusual oxidations, *i.e.*, oxidative addition to organometallic complexes with attack of coordinated carbonyl ligands. However, from earlier work on the reactivity of carbonyl complexes, it seems likely that the first step is oxidation of the low valent metal. Angelici[25] has set the $\nu(C{\equiv}O)$ cutoff for nucleophilic attack of carbonyl ligands at $\approx$2000 cm^{-1}. Carbonyl ligands which exhibit lower $\nu(C{\equiv}O)$ values (including the organometallic substrates examined here) are less susceptible to nucleophilic attack at the carbon atom due to $d\pi$-$p\pi$ back-bonding from the adjacent electron-rich metal center.

The actual oxidation step could occur in several ways; the active oxidant is still a mystery. In CCl_4, the equilibrium constant for the dissociation of pyridine from $OsO_4(py)$ is approximately 12 M^{-1}.[26] In benzene or dichloromethane, similar values should be observed for the dissociation of quinuclidine from $OsO_4(NC_7H_{13})$. Therefore, the oxidation could occur via OsO_4 or $OsO_4(NC_7H_{13})$. From a mechanistic point of view, direct oxo attack, interactions like those proposed by Sharpless,[12] or electron transfer steps are viable pathways. The ring-closure step then is a nucleophilic attack at the carbonyl ligand. This is facilitated by the prior oxidation of the low-valent metal center, which makes the carbonyl ligand

Figure 2.12. Proposed structure for the reaction product of OsO_4 and $Ru(CO)_3(PPh_3)_2$ in the absence of nitrogenous bases.


PPh3
OC
O
O
O
O-C
O
PPh3
CO
Ru
Os
Os
Ru
OC
C-O
O
O
O
CO
O
PPh3
PPh3

more electrophilic (due to the loss of $d\pi$-$p\pi$ back-bonding), and by the anchimeric effect, *i.e.*, intramolecular rather than intermolecular attack.

Reaction of $Pt(PPh_3)_2(C_2H_4)$ with osmium tetraoxide[§] afforded what is believed to be a brown tetranuclear complex (Figure 2.13). Oxidative addition of osmium tetraoxide to the Pt(0) complex resulted in the formation of μ-oxo bridges linking the platinum and osmium atoms. The infrared and ^1H NMR spectroscopic data and the elemental analysis are consistent with this formulation. A molecular weight determination was unsuccessful due to poor solubility in suitable solvents. The ethylene ligand was lost as is the case when $Pt(PPh_3)_2(O_2)$ is formed on aerial oxidation of $Pt(PPh_3)_2(C_2H_4)$.[27]

Complexes with thiocarbonyl, isocyanide, nitrosyl, and dinitrogen ligands have been examined as well. The thiocarbonyl ligands in *trans*-$RhCl(CS)(PPh_3)_2$ and $[Rh(CS)(bpy)(PPh_3)_2]ClO_4$ were not readily attacked on treatment with one equivalent of either osmium tetraoxide or with its quinuclidine adduct; the ν(CS) band in the infrared spectra of the oxidized materials remained. Infrared spectra of the oxidation products of *trans*-$RhCl(CS)(PPh_3)_2$ and osmium(VIII) oxidants exhibited a new sharp band at 1989 cm^{-1}, near the reported value for *trans*-$RhCl(CO)(PPh_3)_2$ (1980 cm^{-1}, CH_2Cl_2).[26] Oxidation with excess equivalents of osmium(VIII) reagents resulted in the decomposition of *trans*-$RhCl(CS)(PPh_3)_2$; no distinct mono- or dioxo osmium vibrations were found in the infrared spectra of the recovered materials. No tractable complexes were obtained on reaction of $[Rh(CN\text{-}t\text{-}Bu)_2(PPh_3)_2]Cl$ with these oxidants.

The nitrosyl complexes $Rh(NO)Cl_2(PPh_3)_2$ and $Rh(NO)(PPh_3)_3$ also did not react cleanly with OsO_4 or $OsO_4(NC_7H_{13})$. The bands in the infrared spectra of the oxidized materials attributable to the NO stretching mode were broad and variable. Degradation of the starting organometallic complexes without the formation of discrete mixed-metal compounds was likely. Oxidation of *trans*-$W(N_2)_2(diphos)_2$ (ν(NN): 1955 cm^{-1}) with osmium tetraoxide afforded a new

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§ The reaction with $OsO_4(NC_7H_{13})$ could not be characterized.

Figure 2.13. Proposed structure for the reaction product of OsO_4 and $Pt(PPh_3)_2(C_2H_4)$ in the absence of nitrogenous bases.


Ph3P
Pt
Ph3P
O
O
Os
O
O
Os
O
O
O
Pt
PPh3
PPh3

complex retaining a coordinated dinitrogen ligand (ν(NN): 2000 cm^{-1}). Unfortunately, elemental analyses were variable and not consistent with any reasonable formulation; infrared bands attributable to oxidized dinitrogen ligands, *e.g.*, the –N=N–O– moiety, were not found.

The oxidations of Co(saltmen),* $Os(CO)_2(PPh_3)_2(C_2H_4)$, and two dimeric species, $\{Mo(\mu\text{-}O_2CCH_3)(thf)Cl\}_2$ and $\{CpMo(CO)_2\}_2$, with osmium(VIII) reagents were found to be ill-defined; no characterizable complexes were obtained. The cyclopentadienyl ligand appeared to be very sensitive to oxidation by osmium tetraoxide; the reactivity of osmium tetraoxide and ferrocene could not be characterized either.

* saltmen = the dianion of *N*,*N*'-(1,1,2,2-tetramethylethylene)bis(salicylideneimine).

Conclusions

We have shown that oxidative addition of osmium tetraoxide·quinuclidine to several organometallic carbonyl complexes results in the formation of μ-CO_2 mixed-metal complexes. The stability of these complexes in solution is thought to be kinetically controlled. The lability of the μ-CO_2 ligand at the ruthenium(II)/-osmium(II) metal center probably facilitates their decomposition, which did not result in characterizable complexes. In the presence of pyridine, however, $(CO)_2$-$(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$, degraded to form $(py)_2OsO_2(\mu\text{-}O)_2$-$OsO_2(py)_2$ (as well as other products). The evolution of carbon dioxide has been demonstrated.

Oxidative addition of osmium tetraoxide to $Ru(CO)_3(PPh_3)_2$, in the absence of nitrogenous bases, again resulted in attack at the coordinated carbonyl ligand with the formation of a μ-CO_2 complex. This molecule was found to be a tetramer; the ruthenium atoms are six-coordinate and the osmium atoms are five-coordinate (Figure 2.12).

One other mode of reactivity has been discovered. Oxidative addition of osmium tetraoxide to $Pt(PPh_3)_2(C_2H_4)$ displaced the ethylene ligand with the formation of μ-oxo bridges connecting the platinum and osmium centers (Figure 2.13). The unusual tetranuclear complex is similar, in many respects, to known dimeric osmium(VI) ester complexes (Figure 2.2a,b).[10]

Oxidation of several other organometallic and inorganic compounds with osmium(VIII) oxidants did not produce tractable products. The oxidative addition of osmium(VIII) reagents does not appear to be applicable to a wide range of compounds; the sensitivity of ligands such as phosphines, nitrosyls, and cyclopentadienyls, to oxidation complicates the reactivity at the low-valent metal center. The reaction of osmium(VIII)-oxo compounds with low valent carbonyl complexes to form μ-CO_2 complexes does not appear to have straightforward analogies in the chemistry of other π-acid ligands such as NO, N_2, CS, and CNR.

Experimental

General Information

Physical and Spectroscopic Methods. Proton NMR spectra were recorded on a Varian 390 spectrometer. The chemical shifts are reported in ppm(δ) relative to tetramethylsilane (δ = 0.0). Solution ^{31}P NMR spectra were recorded on a Jeol FX-90Q spectrometer and solid-state ^{31}P NMR spectra with cross-polarization magic-angle spinning were collected on a Nicolet NT-150 wide-bore spectrometer at the Colorado State University Regional NMR Center.† The chemical shifts are reported in ppm(δ) relative to external H_3PO_4 (δ = 0.0). Infrared spectra were obtained using a Beckman 4240 spectrometer; nujol mulls were routinely used with potassium bromide plates. Elemental analyses were performed by Mr. L. Henling at the C.I.T. Chemistry Dept. Analytical Facility.

Materials. All solvents were reagent grade and used without further purification, except for dichloromethane and tetrahydrofuran which were freshly distilled from calcium hydride and benzene which was freshly distilled from sodium.

The following compounds were used as received: 2,2'-bipyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, ethylenebis(diphenylphosphine), ferrocene, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, $SiCl(CH_3)_3$, triphenylphosphine, WCl_6 (all from the Aldrich Chemical Co.), *t*-butyl isocyanide, $Mo(CO)_6$, OsO_4,‡ K_2PtCl_4, $RhCl_3 \cdot 3H_2O$, $RuCl_3 \cdot xH_2O$ (all from the Alfa Chemical Co.), glacial acetic acid, NH_4Cl, CS_2, HBF_4, $FeCl_2$, Mg, Na, Zn (all from Baker Chemical Co.), formaldehyde (37% w/v), hydrochloric acid (from Malinckrodt Inc.), carbon monoxide, carbon dioxide, molecular oxygen (from the Matheson Co.), $NaBH_4$ from the Wilshire Chemical Co., 3a,4,7,7a-tetrahydro-4,7-methanoindene from MCB Inc., and anhydrous $AgClO_4$ from the G. Frederick Smith Co. Co(saltmen) was a generous gift from Dr. W. P. Schaefer.

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† The Colorado State University Regional NMR Center is funded by the National Science Foundation (Grant No. CHE-8208821).

‡ Several grams of OsO_4 were a gift from the Engelhard Co.

The following compounds were synthesized using reported procedures: $\{CpMo(CO)_2\}_2$,[29] $\{CpMo(CO)_3\}_2$,[30] $Mo_2(\mu\text{-}O_2CCH_3)_4$,[31] $\{MO(\mu\text{-}O_2CCH_3)(thf)Cl\}_2$,[32] $(NH_4)_2[OsCl_6]$,[33] $OsHCl(CO)(PPh_3)_3$,[34] $OsH_2(CO)(PPh_3)_2$,[34] $Os(CO)_2(PPh_3)_3$,[34] $Os(CO)_3(PPh_3)_2$,[35] $Os(CO)_2(PPh_3)_2(C_2H_4)$,[36] $OsO_4(NC_7H_{13})$,[37] $Pt(CO)(PPh_3)_2$,[27] $Pt(PPh_3)_2(C_2H_4)$,[38] $Pt(PPh_3)_3$,[39] $Pt(PPh_3)_4$,[39] $[Rh(CN\text{-}t\text{-}Bu)_2(PPh_3)_2]Cl$,[40] $RhCl(PPh_3)_3$,[41] $RhCl(CS)(PPh_3)_2$,[42] $[Rh(CS)(bpy)(PPh_3)_2]ClO_4$,[43] $Rh(NO)(PPh_3)_3$,[44] $Rh(NO)Cl_2(PPh_3)_2$,[44] $Ru(CO)_3(PPh_3)_2$,[44] $RuHCl(CO)(PPh_3)_2$,[44] $Ru(NO)Cl(CO)(PPh_3)_2$,[45] and $W(N_2)_2(diphos)_2$.[46]

Synthesis

All reactions were run in 100 mL three-neck round bottom flasks under a blanket of flowing high-purity nitrogen unless noted otherwise and all reactions used stoichiometric quantities of osmium(VIII) oxidants and the organometallic/inorganic substrates, except for the study on $RhCl(CS)(PPh_3)_2$ with excess quantities of these reagents. Enrichment with ^{18}O was carried out as follows: The osmium tetraoxide needed for one experiment was placed in a 2 mL round bottom flask along with 40 equivalents of $^{18}OH_2$ (35 μL for 11 mg OsO_4) and 1 drop benzene. The mixture was stirred overnight; then the osmium tetraoxide was dissolved in the solvent required for the experiment. The organic solution was either decanted from the water and used directly, or it was treated with 1 equivalent of quinuclidine, decanted from the water, and then used in the experiment.

Preparation of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})\cdot\frac{1}{3}C_6H_6$ *from benzene.* $Ru(CO)_3(PPh_3)_2$ (39 mg,0.0547 mmol) was placed in the round bottom flask and dissolved in benzene (15 mL). $OsO_4(NC_7H_{13})$ (20 mg,0.0547 mmol), dissolved in benzene (2 mL), was slowly added dropwise. Within 5 minutes the product spontaneously precipitated. It was filtered from the solution, washed with benzene, and dried *in vacuo.* Yield: 47 mg (80%).

Analytical data: $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})\cdot\frac{1}{3}C_6H_6$

IR (cm^{-1},nujol): 2025, 1973 [ss,ν(C≡O)], 1551 [ss,ν(C=O)], 1061 [ss,ν(C–O)], 858 [ss,$\nu(OsO_2)$].

IR (cm^{-1},nujol,^{18}O enriched): 1551 [ss,ν(C=O)], 1046 [ss,ν(C–O)], 816 [ss,$\nu(OsO_2)$].

^1H NMR (CD_2Cl_2): 7.2–7.7 [m,30H,Ph], 7.35 [s,2H,Ph], 2.1–2.5 [m,6H,CH_2], 1.3–1.8 [m,7H,CH_2].

^{31}P NMR (solid-state): 20.6 [s].

E.A.: (Calc.) C: 52.36%, H: 4.12%, N: 1.27%;
(Found) C: 52.28%, H: 4.21%, N: 1.27%.

Preparation of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ *from* CH_2Cl_2. $Ru(CO)_3(PPh_3)_2$ (39 mg,0.0547 mmol) was placed in the round bottom flask and dissolved in CH_2Cl_2 (15 mL). $OsO_4(NC_7H_{13})$ (20 mg,0.0547 mmol), dissolved in CH_2Cl_2 (2 mL), was slowly added dropwise. After 5 minutes, the product was precipitated by addition of hexanes. It was filtered from the solution, washed with hexanes, and dried *in vacuo*. Yield: 50 mg (85%).

Analytical data: $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$
IR (cm^{-1},nujol): 2009, 1955 [ss,ν(C≡O)], 1602 [ss,ν(C=O)], 1038 [ss,ν(C–O)], 852 [ss,$\nu(OsO_2)$].
IR (cm^{-1},nujol,^{18}O enriched): 1602 [ss,ν(C=O)], 1018 [ss,ν(C–O)], 812 [ss,$\nu(OsO_2)$].
^1H NMR (CD_2Cl_2): 7.2–7.7 [m,30H,Ph], 2.1–2.5 [m,6H,CH_2], 1.3–1.8 [m,7H,CH_2].
^{31}P NMR (solid-state): 39.0 [s] (shoulder: 40.5 [s][§]).
E.A.: (Calc.) C: 51.39%, H: 4.03%, N: 1.30%;
(Found) C: 51.28%, H: 4.08%, N: 1.29%.

Decomposition of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$. $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ (120 mg) was dissolved in degassed CH_2Cl_2 which was transfered into the 100 mL round bottom flask using trap-to-trap techniques. The solution was stirred for 24 hours at room temperature. The gases were collected in 67.7 mL with a toepler pump (dry ice/acetone trap). Analysis for CO_2: (Calc.): 30.1 torr, (Found): 39 torr* Carbon dioxide was identified by infrared spectroscopy.

The remaining solution was pumped to dryness *in vacuo*. The infrared spectrum of the crude material contained several bands attributable to carbonyl vibrations, but no strong bands in the 1500–1700 cm^{-1} region or in the 820–890 cm^{-1} region.

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§ This is probably a solid-state artifact.

* Inefficient trapping may have allowed CH_2CL_2 vapor to pass to the pump.

IR (cm^{-1},nujol): 2045, 1982, 1935 [s,ν(C≡O)].

Decomposition of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ *in the presence of pyridine.* $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ (100 mg) was dissolved in degassed CH_2Cl_2 which was transfered into the 50 mL three-necked round bottom flask using trap-to-trap techniques. Then 0.5 mL of pyridine was added via syringe through a septum. The septum was removed under a flow of argon and the flask was stoppered. The solution was immediately frozen, evacuated, then thawed. This step was repeated to remove oxygen, argon, etc. The solution was stirred at room temperature for 24 hours. The gases were collected in 11.6 mL with a toepler pump (dry ice/ethanol trap). Analysis for CO_2: (Calc.): 148.5 torr, (Found): 56.5 torr. Carbon dioxide was identified by infrared spectroscopy.

The remaining solution was pumped to dryness *in vacuo.* The infrared spectrum of this material contained features identical with that of $(py)_2OsO_2(\mu\text{-}O)_2OsO_2(py)_2$, indicating that the crude material contained some of this dimer.

IR (cm^{-1},nujol): 840 [ss,$\nu(OsO_2)$].

Decomposition of $(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ *in the presence of* CS_2. $Ru(CO)_3(PPh_3)_2$ (60 mg,0.0845 mmol) was mixed with $OsO_4(NC_7H_{13})$ in 15 mL of CH_2Cl_2 in a 100 mL round bottom flask. Immediately, 1 mL of CS_2 was added and the flask stoppered. The solution was stirred overnight. Then the crude product was precipitated with hexanes and collected. The infrared spectrum of this material was the same as was found when CS_2 was not present.

IR (cm^{-1},nujol): 2045, 1982, 1935 [s,ν(C≡O)].

Preparation of $(CO)_2(PPh_3)_2Os(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})\cdot\frac{1}{3}C_6H_6$ *from benzene.* $Os(CO)_3(PPh_3)_2$ (44 mg,0.0547 mmol) was placed in the round bottom flask and dissolved in benzene (15 mL). $OsO_4(NC_7H_{13})$ (20 mg,0.0547 mmol),

dissolved in benzene (2 mL), was slowly added dropwise. Within 5 minutes the product spontaneously precipitated. It was filtered from the solution, washed with benzene, and dried *in vacuo*. Yield: 53 mg (83%).

Analytical data: $(CO)_2(PPh_3)_2Os(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})\cdot\frac{1}{3}C_6H_6$
IR (cm^{-1},nujol): 2015, 1952 [ss,ν(C≡O)], 1550 [ss,ν(C=O)],
1068 [ss,ν(C–O)], 861 [ss,$\nu(OsO_2)$].
IR (cm^{-1},nujol,^{18}O enriched): 1550 [ss,ν(C=O)],
1035 [ss,ν(C–O)], 818 [ss,$\nu(OsO_2)$].
^1H NMR (CD_2Cl_2): 7.2–7.7 [m,30H,Ph], 7.35 [s,2H,Ph],
2.1–2.5 [m,6H,CH_2], 1.3–1.8 [m,7H,CH_2].
E.A.: (Calc.) C: 48.44%, H: 3.81%, N: 1.18%;
(Found) C: 48.58%, H: 3.83%, N: 1.14%.

Preparation of $(CO)_2(PPh_3)_2Os(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ *from* CH_2Cl_2. $Os(CO)_3(PPh_3)_2$ (44 mg,0.0547 mmol) was placed in the round bottom flask and dissolved in CH_2Cl_2 (15 mL). $OsO_4(NC_7H_{13})$ (20 mg,0.0547 mmol), dissolved in CH_2Cl_2 (2 mL), was slowly added dropwise. After 5 minutes, the product was precipitated by addition of hexanes. It was filtered from the solution, washed with hexanes, and dried *in vacuo*. Yield: 55 mg (84%).

Analytical data: $(CO)_2(PPh_3)_2Os(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$
IR (cm^{-1},nujol): 2000, 1934 [ss,ν(C≡O)], 1602 [ss,ν(C=O)],
1039 [ss,ν(C–O)], 853 [ss,$\nu(OsO_2)$].
IR (cm^{-1},nujol,^{18}O enriched): 1602 [ss,ν(C=O)],
1018 [ss,ν(C–O)], 810 [ss,$\nu(OsO_2)$].
^1H NMR (CD_2Cl_2): 7.2–7.7 [m,30H,Ph],
2.1–2.5 [m,6H,CH_2], 1.3–1.8 [m,7H,CH_2].
^{31}P NMR (CD_2Cl_2): −0.74 [s].
E.A.: (Calc.) C: 47.46%, H: 3.72%, N: 1.20%;
(Found) C: 47.20%, H: 3.73%, N: 1.16%.

Preparation of $\{(CO)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO(\mu\text{-}O)\}_2\cdot C_6H_6$. $Ru(CO)_3(PPh_3)_2$ (30 mg,0.0433 mmol) was placed in the round bottom flask and dissolved

in benzene (15 mL). OsO_4 (11 mg,0.0433 mmol), dissolved in benzene (2 mL), was slowly added dropwise. After 5 minutes the product was precipitated by addition of hexanes. It was filtered from the solution, washed with hexanes, and dried *in vacuo*. Yield: 31 mg (75%).

Analytical data: $\{(C{\equiv}O)_2(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO(\mu\text{-}O)\}_2{\cdot}C_6H_6$
IR (cm^{-1},nujol): 2020, 1988 [ss,ν(C≡O)], 1622 [ss,ν(C=O)],
—† [ν(C–O)], 972 [ν(OsO)].
IR (cm^{-1},nujol,^{18}O enriched): 1622 [ss,ν(C=O)],
—† [ss,ν(C–O)], 922 [ss,ν(OsO)].
^1H NMR (DMSO-d^6): 7.3–7.7 [m,30H,Ph].
E.A.: (Calc.) C: 50.30%, H: 3.31%.
(Found) C: 50.35%, H: 3.41%.

Preparation of crude $(NO)Cl(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ *from* CH_2Cl_2. $RuCl(NO)(CO)(PPh_3)_2$ (38 mg,0.0547 mmol) was placed in the round bottom flask and dissolved in CH_2Cl_2 (15 mL). $OsO_4(NC_7H_{13})$ (20 mg,0.0547 mmol), dissolved in CH_2Cl_2 (2 mL), was slowly added dropwise. After 5 minutes, the product was precipitated by addition of hexanes. It was filtered from the solution, washed with hexanes, and dried *in vacuo*. Yield: 38 mg (65%).

Analytical data: $(NO)Cl(PPh_3)_2Ru(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$
IR (cm^{-1},nujol): 1804 [ss,ν(NO)], 1630 [ss,ν(C=O)],
1052 [ss,ν(C–O)], 868 [ss,$\nu(OsO_2)$].
IR (cm^{-1},nujol,^{18}O enriched): 1630 [ss,ν(C=O)],
1025 [ss,ν(C–O)], 820 [ss,$\nu(OsO_2)$].

Preparation of crude $(PPh_3)_2Pt(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$ *from* CH_2Cl_2. $Pt(CO)(PPh_3)_2$ (40 mg,0.0547 mmol) was placed in the round bottom flask and dissolved in CH_2Cl_2 (15 mL). $OsO_4(NC_7H_{13})$ (20 mg,0.0547 mmol), dissolved in CH_2Cl_2 (2 mL), was slowly added dropwise. After 2 minutes, the product was

† This band was obscured.

precipitated by addition of hexanes. It was filtered from the solution, washed with hexanes, and dried *in vacuo*. Yield: 43 mg (70%).

Analytical data: $(PPh_3)_2Pt(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$
IR (cm^{-1},nujol): 1612 [ss,ν(C=O)],
—‡ [ν(C–O)], 858 [ss,$\nu(OsO_2)$].
IR (cm^{-1},nujol,^{18}O enriched): 1612 [ss,ν(C=O)],
—‡ [ν(C–O)], 813 [ss,$\nu(OsO_2)$].

Decomposition of $(PPh_3)_2Pt(\mu\text{-}O)(\mu\text{-}CO_2)OsO_2(NC_7H_{13})$. $Pt(CO)(PPh_3)_2$ (40 mg,0.0547 mmol) and $OsO_4(NC_7H_{13})$ (20 mg,0.0547 mmol) were placed in a 100 mL round bottom flask. The reactants were dissolved in CH_2Cl_2 which was transfered into the flask using trap-to-trap vacuum techniques. The solution was stirred for 24 hours at room temperature. Then the gases were collected in 11.6 mL with a toepler pump (dry ice/ethanol trap). Analysis for CO_2: (Calc.) 85.4 torr, (Found) 41.5 torr.

The remaining solution was pumped to dryness *in vacuo*. The infrared spectrum of the crude material contained no strong bands in the 1550–2100 cm^{-1} region and no strong bands in the 820–980 cm^{-1} region.

Preparation of $\{(PPh_3)_2Pt(\mu\text{-}O)_2OsO(\mu\text{-}O)\}_2$. $Pt(PPh_3)_2(C_2H_4)$ (32 mg, 0.0433 mmol) was placed in the round bottom flask and dissolved in benzene (15 mL). OsO_4 (11 mg,0.0433 mmol), dissolved in benzene (2 mL), was slowly added dropwise; the product spontaneously precipitated. It was filtered from the solution, washed with benzene, and dried *in vacuo*. Yield: 32 mg (75%).

Analytical data: $\{(PPh_3)_2Pt(\mu\text{-}O)_2OsO(\mu\text{-}O)\}_2$
IR (cm^{-1},nujol): 965 [ss,ν(OsO)].
IR (cm^{-1},nujol,^{18}O enriched): 915 [ss,ν(OsO)].
^1H NMR (DMSO-d^6): 6.9–7.7 [m,30H,Ph].
E.A.: (Calc.) C: 44.40%, H: 3.10%.

‡ This band was obscured.

(Found) C: 44.54%, H: 3.21%.

Reactivity of trans-$RhCl(CS)(PPh_3)_2$ *with osmium*(VIII) *oxidants.* $RhCl(CS)(PPh_3)_2$ (1 equiv.) was dissolved in CH_2Cl_2 (15 mL). OsO_4, OsO_4 with pyridine (0.5 mL), or $OsO_4(NC_7H_{13})$ (1 equiv.), dissolved in CH_2Cl_2 (2 mL), was then added dropwise with stirring. After 15 minutes, the product was precipitated with hexanes, filtered from the solution, and dried *in vacuo.* The infrared spectra of these materials revealed that the ν(CS) band remained intact. However, a new band formed at 1989 cm^{-1} (nujol).

Reactivity of trans-$RhCl(CS)(PPh_3)_2$ *with excess equivalents of osmium*(VIII) *oxidants.* $RhCl(CS)(PPh_3)_2$ (1 equiv.) was dissolved in CH_2Cl_2 (15 mL). OsO_4 or $OsO_4(NC_7H_{13})$ (2–3 equiv.), dissolved in CH_2Cl_2 (2 mL), was then added dropwise with stirring. The solution darkened considerably. After 15 minutes, the product was precipitated with hexanes, filtered from the solution, and dried *in vacuo.* The infrared spectra of these materials revealed that the ν(CS) band was very broad or gone. No distinct osmium-oxo bands were found.

Reactivity of $[Rh(CS)(bpy)(PPh_3)_2]ClO_4$ *with osmium*(VIII) *oxidants.* $[Rh(CS)(bpy)(PPh_3)_2]ClO_4$ (1 equiv.) was dissolved in CH_2Cl_2 (15 mL). OsO_4 or $OsO_4(NC_7H_{13})$ (1 equiv.), dissolved in CH_2Cl_2 (2 mL), was then added dropwise with stirring. After 15 minutes, the product was precipitated with hexanes, filtered from the solution, and dried *in vacuo.* The infrared spectra of these materials revealed that the ν(CS) band remained intact.

Reactivity of $W(N_2)_2(diphos)_2$ *with* OsO_4. $W(N_2)_2(diphos)_2$ (1 equiv.) was dissolved in degassed benzene (15 mL). OsO_4 (1 equiv.), dissolved in benzene (2 mL), was added dropwise to the solution. A precipitate formed immediately. The product was filtered from the solution, washed with benzene, and dried *in vacuo.*

The infrared spectrum of this material showed a new strong band at 2000 cm^{-1} (nujol).

Reactivity of $Os(CO)_2(PPh_3)_2(C_2H_4)$, $Rh(NO)Cl(CO)(PPh_3)_2$, $Rh(NO)(PPh_3)_3$, $[Rh(t\text{-}BuNC)_2(PPh_3)_2]Cl$, Co(saltmen), $\{Mo(\mu\text{-}O_2CCH_3)(thf)Cl\}_2$, $\{CpMo(CO)_2\}_2$, *and* Cp_2Fe *with osmium*(VIII) *oxidants.* Oxidations were carried out as follows: A solution containing 1 equivalent of OsO_4 or $OsO_4(NC_7H_{13})$ was added dropwise to a solution containing 1 equivalent of the organometallic/inorganic substrate (2 equivalents of Co(saltmen)). The solution was stirred for 2–5 minutes. Addition of hexanes precipitated the reaction products, which were filtered from the solution, washed with hexanes, and dried *in vacuo.* The solvents were typically dichloromethane or benzene; tetrahydrofuran was used for Co(saltmen) oxidations. Infrared spectra exhibited few features attributable to osmium-oxo vibrations. In several instances, broadening of ligand bands was observed. Mixing the reactants together at reduced temperature (−78°C) and then warming the products to room temperature was also ineffective in improving the reactivity. When attempted, heating the reaction solutions was also not productive.

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Appendix A. Structure factor amplitudes ($10F_o$, $10F_c$, $10\sigma_F$; $\sigma_F/k = [F_o + \sigma_{F^2}]^{\frac{1}{2}} - |F_o|$, k = 0.3100; $F_o < 0$ means $I_o < 0$) for $(H)_4$CHBA-Et·pyHCl.

```
 -14    Ø  L
1     43   -33     9
 -14    1  L
1     69   -34    17
 -14    2  L
1     -4     8    -4
 -14    3  L
1     49    52    -5
 -13    Ø  L
1    -12   -31   -15
2     76   -72     6
3      Ø     6     Ø
 -13    1  L
1    1Ø2   -65     3
2     51    31   -11
3     25    -5     3
 -13    2  L
1    -13    11    -7
2     36     1    14
3    11Ø    97    -1
 -13    3  L
1     -3     Ø   -12
2    125   1Ø7     3
3    1Ø6    92    24
 -13    4  L
1     47   -18    -2
2     52   -27    -4
 -13    5  L
1     45   -28     4
2     27   -31   -15
 -13    6  L
1     46    49   -2Ø
2     68    61    -3
 -13    7  L
1      6    -2    -3
2    112   118   -18
 -13    8  L
1     32   -31     Ø
2     39     8    -4
 -13    9  L
1     65   -17    -1
2     4Ø    11    15
 -13   1Ø  L
1    -21    25   -21
 -13   11  L
1     53    36     4
 -12    Ø  L
1     46    41     6
2    -28    -4   -12
3     52    34    19
 -12    1  L
1    114   1Ø5   -12
2     8Ø    86   -18
3     23    38   -17
 -12    2  L
1     9Ø     Ø    -8
2     86   -25     6
3     29    -8    -1
 -12    3  L
1     92   -87     4
2     77   -48     Ø
3     86   -61    -3
 -12    4  L
1     6Ø     5     2
2     25   -18    -3
3     48    4Ø     9
 -12    5  L
1    1ØØ   -14    -6
2     47    34    12
3    1Ø8    67    15
 -12    6  L
1     61   -35     2
2    1Ø1   -91   2Ø
3     74    64    19
 -12    7  L
1     75   -54    12
2     29   -3Ø   -1Ø
3     35     1    13
 -12    8  L
1     17     Ø     1
2     73   -22    14
3     41   -35    -6
 -12    9  L
1     84    -8   -12
2    149   137    17
3     93    91     4
 -12   1Ø  L
1     33    17     1
2     86    81     5
3     25    -5    -6
 -12   11  L
1    162  -158    -7
2     67   -57   -17
 -12   12  L
1     44   -18    -6
2     61    12   -14
 -12   13  L
1    122   112     8
2     52    3Ø     6
 -12   14  L
1      5    21    -7
2     49    5Ø   -14
 -12   15  L
1     69    13   -21
 -11    Ø  L
1     38    4Ø    -2
2     28    19     6
3    1Ø1    99     4
4    158   156     4
 -11    1  L
1    16Ø   -53   -18
2     88   -57   -18
3     71    22    24
4     2Ø    13     3
 -11    2  L
1    118   -48   2Ø
2    1Ø2   -51    13
3     92   -94   -12
4     45    15     Ø
 -11    3  L
1     83   -47     2
2     3Ø     6     5
3    161   131    -7
4     55    12     Ø
 -11    4  L
1     86    39   -17
2     53    58   -14
3     54   -36    26
4     59    17     Ø
 -11    5  L
1    178  -178    -1
2     7Ø   -75   -16
3     77    58     3
4     44   -34     7
 -11    6  L
1     5Ø    -6   -18
2     42    12   -22
3     74    44    1Ø
4     9Ø   -54   -1Ø
 -11    7  L
1     86    6Ø    23
2     1Ø    -7     Ø
3     52    62   -2Ø
4     35    3Ø     Ø
 -11    8  L
1    12Ø    51   -26
2     2Ø    18    -9
3     81    37     Ø
4     41   -38    -1
 -11    9  L
1     94    -8   -16
2     86   -83     8
3     29    19     8
4     38    25     Ø
 -11   1Ø  L
1     6Ø   -4Ø   -11
2     47   -45     Ø
3     45   -49    -9
 -11   11  L
1     76    76     Ø
2     7Ø    -3   -1Ø
3     28    -8    13
 -11   12  L
1      7     Ø     Ø
2     31    25    -6
3    1ØØ    97     5
 -11   13  L
1     67   -49    -9
2     35   -38    -8
3     51    24    -8
 -11   14  L
1     7Ø   -62     1
2    115   -9Ø   -12
3     83   -31    26
 -11   15  L
1    124    73    24
2     55    46    1Ø
 -11   16  L
1     48    42     7
2     68    68    -1
 -11   17  L
1     76   -78    -7
2    -21   -1Ø   -13
 -11   18  L
1     33   -3Ø    -7
 -1Ø    Ø  L
1     46    39     8
2    147   156   -22
3     55   -52     4
4     3Ø   -24     4
 -1Ø    1  L
1    212   -73   -1Ø
2    139    -8     3
3     7Ø   -16    -9
4     4Ø   -34   -14
 -1Ø    2  L
1    1Ø7    31    11
2    114    27   -23
3     67   -36     7
4     11    15    -1
 -1Ø    3  L
1     65   -6Ø   -1Ø
2    127   -33     9
3     31   -28    -2
4     76    59    1Ø
 -1Ø    4  L
1    1Ø4   -76    11
2    186   -77    -5
3     82   -74    12
4     4Ø   -26     4
 -1Ø    5  L
1     2Ø    15    -1
2    125  -126    -6
3    11Ø   -77   -2Ø
4    121    26     6
 -1Ø    6  L
1    146   133   -18
2     99    91   -12
3     18    17   -13
4     98    81    17
 -1Ø    7  L
1     7Ø   -37     Ø
2     37   -3Ø     9
3    136   118     6
4     52    39    19
 -1Ø    8  L
1     48   -42     4
2    168  -13Ø    -4
3    131   -55     1
4     48    33    -4
 -1Ø    9  L
1    119   -98     Ø
2    129   -91    -6
3     31     2    -8
4    -18     Ø    -9
 -1Ø   1Ø  L
1     95    55   -12
2     64    11   -12
3     72    59    -9
4     44    -7     2
 -1Ø   11  L
1     23   -29    -8
2     62    -3   -17
3     68    61    13
4    115   1Ø4     9
```

-10 12 L

1 71 -48 6
2 35 22 14
3 30 20 6
4 90 -79 19

-10 13 L

1 85 77 7
2 76 -34 -9
3 75 -44 3
4 92 -74 -1

-10 14 L

1 46 -40 -20
2 135 54 -9
3 113 106 -10

-10 15 L

1 107 87 -26
2 75 57 -17
3 27 40 -14

-10 16 L

1 89 -87 -14
2 130 -99 -16
3 67 -44 10

-10 17 L

1 28 2 16
2 34 14 -5
3 93 -73 9

-10 18 L

1 63 52 0
2 58 27 25

-10 19 L

1 74 -56 1
2 10 27 -15

-10 20 L

1 62 -28 4

-9 0 L

1 112 117 -11
2 225 -226 -1
3 28 33 -4
4 58 55 3
5 108 101 13

-9 1 L

1 218 157 -12
2 248 71 -10
3 73 -23 -7
4 84 26 -20
5 -7 -7 -2

-9 2 L

1 145 -38 -7
2 185 58 -5
3 41 29 15
4 37 -34 2
5 34 18 4

-9 3 L

1 189 -183 5
2 194 -184 -22
3 105 -103 3
4 35 33 1
5 58 -55 -1

-9 4 L

1 248 -169 -5
2 203 88 -9
3 59 -30 -8
4 43 -36 2
5 50 -28 11

-9 5 L

1 218 53 14
2 99 91 -2
3 129 107 24
4 167 162 7
5 48 14 12

-9 6 L

1 118 91 -14
2 96 21 0
3 83 29 -4
4 38 11 22
5 64 -9 0

-9 7 L

1 98 81 -22
2 90 -90 0
3 270 -268 -11
4 64 -46 -3
5 39 9 0

-9 8 L

1 177 64 -5
2 117 99 0
3 49 44 0
4 108 -54 3
5 45 -32 16

-9 9 L

1 206 162 13
2 153 105 -9
3 41 -19 -15
4 96 70 -9

-9 10 L

1 156 -138 0
2 176 -58 -18
3 87 -88 -5
4 71 10 20

-9 11 L

1 96 4 9
2 69 -24 5
3 115 -83 -19
4 30 -15 11

-9 12 L

1 125 126 -5
2 55 -25 -2
3 77 -21 -2
4 115 111 4

-9 13 L

1 113 61 -4
2 72 78 -16
3 74 -11 -4
4 47 18 -27

-9 14 L

1 66 21 -1
2 99 -83 8
3 15 6 1
4 24 15 -5

-9 15 L

1 134 -93 1
2 51 -32 7
3 25 23 1
4 110 -33 29

-9 16 L

1 71 -26 6
2 108 -74 -15
3 54 36 -11

-9 17 L

1 38 -11 6
2 13 25 -15
3 139 137 4

-9 18 L

1 110 13 20
2 18 -1 -14
3 40 24 -8

-9 19 L

1 74 -67 -2
2 94 -90 11
3 62 -67 -9

-9 20 L

1 120 -23 -4
2 101 69 10

-9 21 L

1 35 34 -10
2 81 77 -2

-9 22 L

1 49 -40 0

-8 0 L

1 97 -103 -15
2 47 -34 14
3 163 163 0
4 33 30 3
5 38 -35 3

-8 1 L

1 201 -189 -5
2 403 -326 -2
3 286 -164 5
4 66 -39 1
5 92 66 -20

-8 2 L

1 407 -102 19
2 214 -54 -5
3 78 2 18
4 127 -125 0
5 59 -19 13

-8 3 L

1 346 306 23
2 133 78 21
3 162 -42 -16
4 97 -65 7
5 54 45 5

-8 4 L

1 73 70 -1
2 113 93 3
3 112 60 17
4 67 -50 -9
5 82 44 15

-8 5 L

1 125 6 -14
2 87 71 -14
3 116 -85 -2
4 49 -10 -5
5 67 24 11

-8 6 L

1 83 -76 -5
2 87 -84 8
3 85 -16 -19
4 67 59 16
5 30 -31 -8

-8 7 L

1 158 159 -4
2 38 -22 14
3 175 -135 -21
4 69 52 0
5 45 44 0

-8 8 L

1 231 133 -13
2 112 89 0
3 51 -59 -18
4 40 39 -6
5 62 53 6

-8 9 L

1 77 -7 -10
2 171 -132 -13
3 85 -82 5
4 31 -25 2
5 33 9 -5

-8 10 L

1 56 -61 -17
2 37 36 -1
3 75 -47 -17
4 82 -65 2
5 -22 4 -10

-8 11 L

1 63 53 14
2 124 123 1
3 187 166 -19
4 57 57 0
5 21 -15 2

-8 12 L

1 71 46 14
2 45 37 -1
3 90 89 -16
4 68 64 7

-8 13 L

1 -15 1 -8
2 86 -93 -31
3 166 -140 0
4 -17 -4 -7

-8 14 L

1 91 21 27
2 18 -20 -1
3 36 -58 -38
4 35 13 -5

-8 15 L

1 142 140 -1
2 140 128 -27
3 -19 0 -8
4 39 -22 18

-8 16 L

1 33 31 2
2 31 -19 -20
3 51 -45 8
4 -1 17 -14

-8 17 L

1 96 -89 3
2 55 11 -8
3 52 57 -22
4 35 -25 4

-8 18 L

1 37 29 9
2 137 -146 -29
3 53 -50 -1

-8 19 L

1 73 -55 -3
2 58 -58 -2
3 120 4 36

-8 20 L

1 131 134 -25
2 39 25 8
3 5 6 -1

-8 21 L

1 105 -103 5
2 96 -71 2
3 30 -19 7

-8 22 L

1	99	-90	-14
2	100	33	11

-8 23 L

1	45	33	13
2	39	44	-15

-8 24 L

1	61	-36	-3

-7 0 L

1	299	-294	12
2	329	-324	10
3	71	-79	-15
4	47	-49	-3
5	57	-53	5

-7 1 L

1	124	-104	17
2	315	-248	-1
3	147	-35	8
4	39	-9	11
5	39	-40	-20

-7 2 L

1	178	119	-3
2	92	1	-22
3	53	40	-5
4	120	118	5
5	65	55	7

-7 3 L

1	223	-201	0
2	63	-50	21
3	141	77	10
4	71	5	5
5	28	34	-7

-7 4 L

1	141	-135	4
2	78	-60	0
3	55	-25	2
4	-19	-2	-8
5	50	-27	14

-7 5 L

1	165	57	38
2	317	274	-22
3	69	53	2
4	160	-154	-4
5	58	22	4

-7 6 L

1	155	-131	-1
2	107	108	-17
3	208	209	-11
4	44	-38	7
5	83	-58	6

-7 7 L

1	204	-162	11
2	177	-47	-2
3	74	68	5
4	70	-61	6
5	49	33	18

-7 8 L

1	123	-94	11
2	40	-28	-1
3	197	15	6
4	49	-36	21
5	43	-35	10

-7 9 L

1	53	44	3
2	196	95	28
3	58	-40	9
4	156	-153	-6
5	33	-12	17

-7 10 L

1	271	228	5
2	103	82	-14
3	99	-50	5
4	103	6	-8
5	139	67	38

-7 11 L

1	37	30	2
2	309	239	-10
3	100	42	-4
4	84	-52	-4
5	89	83	11

-7 12 L

1	73	-46	14
2	21	-11	0
3	101	-52	12
4	41	-49	-16
5	15	12	0

-7 13 L

1	73	-24	9
2	97	-79	-5
3	114	29	-9
4	65	-4	-18
5	58	-58	-2

-7 14 L

1	188	189	-16
2	30	14	-26
3	73	-76	-10
4	71	68	1
5	47	28	-9

-7 15 L

1	140	-43	3
2	219	-135	11
3	14	-8	-20
4	113	100	27

-7 16 L

1	41	7	-20
2	45	-6	5
3	141	-121	2
4	13	16	-8

-7 17 L

1	19	28	-9
2	58	61	-12
3	19	-2	4
4	9	16	-3

-7 18 L

1	109	-48	-11
2	64	67	-11
3	23	29	-6
4	34	-43	-12

-7 19 L

1	52	-34	-4
2	93	-89	-10
3	38	41	-10
4	48	41	5

-7 20 L

1	44	-53	-20
2	8	-26	-15
3	49	21	11

-7 21 L

1	99	88	5
2	70	-65	5
3	69	-60	1

-7 22 L

1	127	119	1
2	68	57	-5
3	54	28	-5

-7 23 L

1	14	-4	-3
2	104	98	-3

-7 24 L

1	77	-54	4
2	70	-60	9

-7 25 L

1	47	-13	-4

-6 0 L

1	266	-261	13
2	-28	12	-18
3	234	-238	-9
4	18	23	-3
5	91	-98	-13
6	-6	16	-4

-6 1 L

1	224	-217	-13
2	217	60	-8
3	163	146	13
4	192	7	-18
5	42	0	11
6	86	51	9

-6 2 L

1	217	-200	-19
2	105	-82	-7
3	258	0	-6
4	87	73	25
5	66	-49	4
6	49	-11	32

-6 3 L

1	393	-275	22
2	21	8	8
3	244	-22	10
4	180	-144	4
5	86	-57	7
6	42	25	1

-6 4 L

1	438	324	26
2	151	-11	7
3	121	88	13
4	77	39	-15
5	64	35	11
6	36	-15	9

-6 5 L

1	139	3	44
2	337	309	11
3	79	72	12
4	53	-43	-7
5	63	43	38
6	0	21	-9

-6 6 L

1	155	120	67
2	100	-49	-19
3	117	-106	-4
4	76	-44	10
5	-9	14	-12

-6 7 L

1	373	-353	-19
2	14	-32	-29
3	55	-49	-18
4	202	-142	-9
5	65	-32	23

-6 8 L

1	139	127	9
2	205	4	-9
3	55	43	-35
4	130	40	9
5	30	7	18

-6 9 L

1	151	-91	15
2	91	7	-19
3	177	173	9
4	92	84	-3
5	31	-11	9

-6 10 L

1	76	74	-18
2	95	31	10
3	114	103	-16
4	47	19	-7
5	-9	3	-6

-6 11 L

1	96	-15	5
2	66	-54	3
3	125	-90	5
4	54	-43	-16
5	42	-29	-6

-6 12 L

1	135	-119	12
2	91	62	-13
3	52	48	-6
4	59	-67	-21
5	47	0	11

-6 13 L

1	149	55	-6
2	243	230	2
3	138	83	0
4	37	35	-9
5	82	69	8

-6 14 L

1	154	-154	-3
2	103	103	-20
3	143	61	-11
4	152	-75	-9
5	27	-22	4

-6 15 L

1	50	-21	10
2	100	-90	17
3	102	-103	-23
4	112	-113	-3
5	78	-68	20

-6 16 L

1	97	-12	3
2	19	8	-12
3	48	-53	-30
4	86	11	-2

-6 17 L

1	232	217	-1
2	94	81	9
3	63	48	-22
4	75	60	5

-6 18 L

1	78	-70	-21
2	78	-20	-1
3	142	-147	-15
4	47	-42	-7

-6 19 L

1	52	-27	0
2	80	-66	1
3	84	-71	-5
4	35	-26	4

-6 20 L

1	57	50	4
2	68	71	-17
3	28	15	0
4	68	-50	34

-6 21 L

1	65	-35	-4
2	104	-101	2
3	93	29	10

-6 22 L

1	46	10	13
2	63	-10	16
3	88	68	4

-6 23 L

1	110	107	9
2	73	-65	0
3	57	-50	4

-6 24 L

1	35	-34	0
2	26	-34	-16

-6 25 L

1	38	34	-3
2	54	40	-10

-6 26 L

1	19	-17	0

-5 0 L

1	309	319	-27
2	99	-96	8
3	316	-307	19
4	19	21	-1
5	95	95	0
6	54	-50	4

-5 1 L

1	140	-120	17
2	365	-179	-11
3	207	-52	0
4	35	-7	-13
5	42	18	4
6	29	8	8

-5 2 L

1	166	156	-29
2	260	-232	4
3	209	-188	11
4	81	6	11
5	48	37	12
6	39	23	3

-5 3 L

1	200	100	14
2	161	-30	29
3	213	199	-9
4	167	160	0
5	50	-42	-8
6	43	-25	-2

-5 4 L

1	391	344	27
2	276	100	51
3	330	181	-1
4	133	129	8
5	64	-26	19
6	26	9	11

-5 5 L

1	139	-69	55
2	437	-434	3
3	88	-61	10
4	107	79	-7
5	147	-133	19
6	47	-28	14

-5 6 L

1	195	-164	30
2	200	-202	-13
3	129	-123	4
4	-13	3	-15
5	61	-31	41
6	70	-55	9

-5 7 L

1	223	193	58
2	150	120	33
3	231	212	-3
4	104	90	-9
5	64	-57	15
6	-5	25	-14

-5 8 L

1	194	113	16
2	117	106	7
3	196	112	-24
4	27	7	-4
5	28	0	3

-5 9 L

1	369	-358	8
2	224	-52	9
3	102	7	15
4	74	-73	-2
5	108	-90	-8

-5 10 L

1	33	30	-7
2	154	52	27
3	129	128	-3
4	74	-16	5
5	52	-46	-3

-5 11 L

1	105	93	9
2	101	106	-19
3	146	83	-12
4	120	67	-12
5	30	-18	10

-5 12 L

1	60	-23	2
2	54	33	6
3	102	-92	0
4	64	-45	3
5	56	54	0

-5 13 L

1	105	-60	15
2	178	-120	-8
3	136	-59	-27
4	67	-25	3
5	20	27	-6

-5 14 L

1	116	-103	24
2	145	67	-3
3	41	-22	-14
4	88	-85	0
5	30	24	0

-5 15 L

1	268	41	1
2	58	18	-13
3	71	46	-5
4	22	18	1
5	83	30	12

-5 16 L

1	199	-171	-5
2	69	54	0
3	134	133	-15
4	33	-28	-11
5	-28	-16	-23

-5 17 L

1	168	-129	7
2	125	-116	7
3	100	-101	-15
4	41	13	-6

-5 18 L

1	269	-276	-33
2	73	-66	-21
3	84	-10	2
4	85	-19	2

-5 19 L

1	87	91	-15
2	152	155	-8
3	-16	31	-29
4	50	43	-3

-5 20 L

1	80	-24	5
2	131	95	-18
3	173	55	10
4	-29	-3	-18

-5 21 L

1	66	-35	4
2	53	8	-6
3	70	-60	-11
4	76	-82	-15

-5 22 L

1	88	6	-7
2	41	-14	2
3	46	44	4

-5 23 L

1	49	48	-7
2	62	60	-6
3	39	34	-8

-5 24 L

1	94	81	23
2	26	-9	-4
3	5	-13	-4

-5 25 L

1	56	-7	10
2	91	-24	23

-5 26 L

1	68	55	22
2	34	-15	1

-5 27 L

1	38	16	2

-4 0 L

1	288	-290	-3
2	647	-655	-11
3	210	-203	16
4	41	-29	12
5	27	-17	6
6	46	-1	29

-4 1 L

1	531	520	16
2	419	391	25
3	96	34	2
4	81	67	-16
5	159	-99	13
6	27	-15	5

-4 2 L

1	407	401	16
2	221	144	5
3	126	116	29
4	45	-42	5
5	74	30	7
6	46	-27	-4

-4 3 L

1	382	-321	31
2	291	-124	41
3	-7	3	-12
4	250	135	-4
5	49	-16	5
6	64	52	14

-4 4 L

1	352	-65	41
2	170	124	-18
3	34	-16	-3
4	198	-128	-12
5	83	38	-8
6	69	-10	10

-4 5 L

1	240	13	45
2	186	-166	29
3	120	110	9
4	77	-64	14
5	110	-73	17
6	52	-37	0

-4 6 L

1	283	245	5
2	216	165	67
3	194	-100	-8
4	70	57	-8
5	54	35	10
6	43	38	-8

-4 7 L

1	684	398	26
2	298	-236	11
3	86	-34	12
4	90	79	-13
5	49	9	5
6	26	-19	2

-4 8 L

1	581	-175	19
2	202	72	-8
3	233	-122	5
4	73	60	7
5	74	-1	16
6	42	-13	8

-4 9 L

1	364	258	23
2	208	-190	21
3	19	0	1
4	154	151	-12
5	98	8	-11
6	-11	-14	-6

-4 10 L

1	103	64	-8
2	239	236	-17
3	218	162	16
4	51	46	-12
5	25	15	2

-4 11 L

1	211	-149	2
2	218	-213	8
3	62	54	17
4	151	-1	7
5	63	-53	20

-4 12 L

1	419	-410	1
2	266	-262	14
3	170	92	-15
4	24	35	-15
5	82	-67	2

-4 13 L

1	257	164	2
2	127	59	4
3	88	61	4
4	100	-11	-21
5	36	-4	8

-4 14 L

1	150	-49	-12
2	57	17	-10
3	87	77	12
4	44	47	-7
5	61	-48	0

-4 15 L

1	265	1	-6
2	151	93	-13
3	24	-15	-15
4	71	-73	-11
5	23	6	-8

-4 16 L

1	147	-95	-6
2	122	-96	-14
3	101	-28	-11
4	65	-51	8
5	46	-43	-13

-4 17 L

1	270	-135	-10
2	116	115	-14
3	54	22	1
4	79	-76	1
5	73	-54	-4

-4 18 L

1	155	83	1
2	124	-105	-24
3	-3	23	-17
4	23	-3	8

-4 19 L

1	61	-47	20
2	78	60	-19
3	10	-18	-11
4	68	52	3

-4 20 L

1	-27	-13	-47
2	77	-46	7
3	73	-57	0
4	58	-37	-9

-4 21 L

1	88	73	0
2	62	62	0
3	51	-48	6
4	79	-8	-3

-4 22 L

1	92	91	-9
2	115	114	1
3	75	38	2
4	-3	17	-17

-4 23 L

1	106	-105	-7
2	37	-44	-17
3	68	-45	7

-4 24 L

1	81	-74	-29
2	103	-73	3
3	24	-2	-4

-4 25 L

1	88	48	24
2	88	86	0
3	30	1	0

-4 26 L

1	23	39	-18
2	61	30	12

-4 27 L

1	49	-31	14
2	40	15	10

-4 28 L

1	45	11	-3

-3 0 L

1	64	-61	8
2	339	343	-10
3	42	-35	10
4	135	-130	11
5	188	197	-20
6	26	34	-6

-3 1 L

1	649	405	35
2	142	79	-2
3	227	127	-21
4	188	185	-12
5	129	121	10
6	10	21	-7

-3 2 L

1	488	122	-32
2	248	246	-3
3	320	-218	0
4	186	-184	5
5	87	8	9
6	32	9	16

-3 3 L

1	480	371	36
2	92	-67	-23
3	216	-208	7
4	257	39	0
5	79	32	-10
6	102	-79	-1

-3 4 L

1	321	96	70
2	403	335	-5
3	80	-71	-7
4	171	35	21
5	92	-21	13
6	43	11	6

-3 5 L

1	226	-34	-1
2	21	0	15
3	154	-147	13
4	151	147	-6
5	104	105	-4
6	66	-59	10

-3 6 L

1	645	-659	-30
2	14	-14	0
3	96	96	-1
4	78	49	-30
5	43	42	-4
6	40	-18	21

-3 7 L

1	267	190	-5
2	69	-10	-3
3	141	-126	11
4	190	-21	-11
5	53	-2	5
6	51	-48	-16

-3 8 L

1	394	262	0
2	98	-37	34
3	219	111	-5
4	54	-57	-7
5	32	-24	9
6	42	-22	-10

-3 9 L

1	71	57	-13
2	76	64	24
3	284	130	19
4	177	95	4
5	47	42	7
6	-29	-9	-19

-3 10 L

1	186	-64	-11
2	105	-23	15
3	232	22	-5
4	92	89	4
5	33	-31	0
6	-25	16	-19

-3 11 L

1	206	-157	13
2	131	-125	15
3	161	-110	0
4	107	-68	9
5	52	-18	9

-3 12 L

1	192	71	-25
2	100	68	12
3	128	-111	-10
4	43	35	3
5	40	-28	16

-3 13 L

1	201	96	-3
2	61	-46	-42
3	64	-27	-19
4	128	8	16
5	34	25	-5

-3 14 L

1	262	78	8
2	232	-232	0
3	121	39	6
4	-5	7	-7
5	71	-24	-4

-3 15 L

1	100	30	-10
2	149	-149	-45
3	112	-31	4
4	77	38	3
5	15	2	2

-3 16 L

1	328	324	-2
2	308	-290	-3
3	99	48	-39
4	60	14	-6
5	27	11	11

-3 17 L

1	37	-55	-29
2	132	-89	-43
3	20	10	-8
4	62	7	-1
5	43	24	19

-3 18 L

1	202	-141	-5
2	131	-135	-27
3	42	35	11
4	85	85	-5
5	18	-20	-3

-3 19 L

1	181	3	0
2	121	45	-28
3	39	45	-15
4	105	-49	8

-3 20 L

1	56	-49	12
2	56	14	0
3	63	30	-11
4	105	54	31

-3 21 L

1	41	-38	5
2	118	107	17
3	105	102	-9
4	64	59	7

-3 22 L

1	8	8	-7
2	47	-45	-13
3	66	-20	7
4	32	-17	8

-3 23 L

1	130	-77	-5
2	64	12	-2
3	60	-39	3

-3 24 L

1	92	10	16
2	125	93	13
3	32	33	-17

-3 25 L

1	-4	-4	-3
2	51	31	1
3	56	62	-26

-3 26 L

1	87	-61	15
2	82	70	22

-3 27 L

1	37	26	3
2	37	0	-1

-3 28 L

1	36	3	3

-2 0 L

1	185	-178	23
2	263	265	-4
3	47	-37	17
4	87	94	-17
5	36	43	-9
6	-9	11	-3

-2 1 L

1	161	-97	-17
2	352	100	33
3	133	86	12
4	66	-66	-7
5	37	-27	6
6	-14	1	-5

-2 2 L

1	474	-228	38
2	263	-69	-17
3	21	-19	-12
4	111	-24	-2
5	121	-88	0
6	46	-6	22

-2 3 L

1	50	-36	15
2	274	257	-9
3	290	265	-7
4	54	47	14
5	77	63	17
6	27	-10	5

-2 4 L

1	319	-151	-8
2	491	59	0
3	200	95	17
4	79	-86	-21
5	73	-71	-8
6	24	20	-7

-2 5 L

1	406	-233	14
2	408	-103	23
3	264	-234	28
4	135	-115	17
5	79	36	-20
6	51	-30	19

-2 6 L

1	326	-144	63
2	347	335	17

3	53	11	23
4	174	-5Ø	-2
5	92	66	32
6	42	39	-6

-2 7 L

1	4Ø5	336	-29
2	564	398	-9
3	258	-53	11
4	56	56	-1
5	146	94	6
6	34	3Ø	4

-2 8 L

1	51	-34	4Ø
2	129	127	-14
3	1Ø9	47	29
4	81	49	15
5	21	31	-11
6	37	11	24

-2 9 L

1	83	88	-21
2	8Ø	18	-2
3	318	-291	2Ø
4	11	-15	-2
5	43	29	-8
6	28	-21	6

-2 1Ø L

1	61	-56	Ø
2	628	-483	16
3	85	-17	-7
4	158	19	4
5	26	2	9
6	93	-3Ø	21

-2 11 L

1	259	193	1Ø
2	185	9Ø	-9
3	64	-38	-5
4	128	115	-12
5	8Ø	56	Ø
6	43	-47	-1Ø

-2 12 L

1	189	177	-2
2	137	-8	-4
3	229	212	-36
4	113	96	6
5	67	62	-6

-2 13 L

1	181	-71	2Ø
2	1Ø8	-1Ø8	-23
3	128	-136	-27
4	96	-72	-14
5	67	-52	-17

-2 14 L

1	-3Ø	-7	-24
2	4Ø5	-215	-1Ø
3	2Ø7	-217	-36
4	14	-22	-1Ø
5	43	-33	6

-2 15 L

1	123	32	12
2	4Ø7	257	-17
3	263	174	Ø
4	5Ø	27	2
5	78	-51	27

-2 16 L

1	174	15Ø	13
2	-22	-34	-39
3	8Ø	-3Ø	-18
4	1Ø3	87	-9
5	15	-16	-1

-2 17 L

1	224	-222	8
2	142	-141	-3
3	67	-24	2
4	42	-38	-12
5	5	-26	-13

-2 18 L

1	232	232	-3
2	141	-17	-14
3	83	-68	-11
4	87	-61	13
5	59	48	-12

-2 19 L

1	113	9	6
2	55	-12	-12
3	142	133	6
4	21	28	-8

-2 2Ø L

1	124	1Ø3	1Ø
2	134	64	1Ø
3	73	-49	-6
4	49	-59	-17

-2 21 L

1	112	4	-2
2	24	-21	1
3	56	47	Ø
4	52	-32	8

-2 22 L

1	164	-86	12
2	5Ø	1Ø	-2
3	56	-7	Ø
4	34	41	-9

-2 23 L

1	5Ø	-32	-21
2	91	-94	-8
3	43	-3	Ø
4	5Ø	35	-13

-2 24 L

1	2Ø	-1Ø	4
2	49	21	-1Ø
3	34	26	6

-2 25 L

1	47	2	12
2	24	-25	-2
3	4Ø	14	-3

-2 26 L

1	34	-3Ø	3
2	83	-4	-15
3	56	41	Ø

-2 27 L

1	-25	11	-21
2	47	45	Ø

-2 28 L

1	67	-55	12
2	-37	8	-26

-1 Ø L

1	377	385	-19
2	83	-83	-1
3	142	139	1Ø
4	74	-73	2
5	-12	6	-3
6	6Ø	53	9

-1 1 L

1	234	244	-7Ø
2	348	358	-58
3	91	-36	-16
4	32	-25	-13
5	115	87	15
6	-9	5	-5

-1 2 L

1	18Ø	-9Ø	-9
2	226	2Ø9	-1Ø
3	319	317	-11
4	157	-92	-26
5	8Ø	-67	13
6	46	54	-15

-1 3 L

1	462	443	-32
2	248	55	-38
3	1ØØ	-1Ø8	-31
4	151	-77	Ø
5	87	81	4
6	22	22	-6

-1 4 L

1	1127	-1141	-18
2	569	-367	-11
3	59	15	-17
4	82	-69	-24
5	124	-112	17
6	-12	3	-6

-1 5 L

1	621	88	-33
2	14Ø	-95	4
3	169	11Ø	-8
4	47	54	-25
5	37	4Ø	-9
6	3Ø	16	11

-1 6 L

1	943	8Ø8	-36
2	248	39	3Ø
3	148	148	-16
4	195	191	1Ø
5	44	42	3
6	38	-33	1

-1 7 L

1	234	-233	-28
2	244	236	7
3	1Ø8	-11Ø	-13
4	12Ø	-112	7
5	1Ø3	52	14
6	1Ø	3Ø	-17

-1 8 L

1	457	-161	-44
2	446	-4Ø9	-12
3	24	4	12
4	35	-19	18
5	48	14	6
6	38	-13	5

-1 9 L

1	244	237	23
2	362	357	6
3	121	1Ø3	2
4	84	-92	-27
5	31	-23	4
6	29	6	14

-1 1Ø L

1	71	18	-7
2	286	242	1
3	143	43	3
4	122	-39	-3
5	59	-21	21
6	27	1	-4

-1 11 L

1	377	-37Ø	-12
2	357	-338	Ø
3	58	-36	-26
4	-21	3	-13
5	31	-8	-2
6	38	25	6

-1 12 L

1	196	2Ø2	-44
2	181	171	Ø
3	289	-292	-8
4	65	-3	Ø
5	44	45	-5

-1 13 L

1	29Ø	2Ø2	-1Ø
2	371	344	-11
3	144	-139	-2
4	6Ø	-56	-5
5	28	4	9

-1 14 L

1	272	168	-3
2	187	17Ø	Ø
3	144	-1Ø1	-4Ø
4	25	-17	3
5	89	7Ø	-5

-1 15 L

1	25	7	4
2	38	-35	-13
3	26Ø	-25Ø	-7
4	48	-24	Ø
5	4Ø	32	3

-1 16 L

1	175	-116	1
2	38	-33	7
3	131	-122	16
4	43	-37	4
5	-8	3	-13

-1 17 L

1	119	116	4
2	2Ø9	-144	-12
3	171	94	-7
4	1Ø2	11Ø	-37
5	61	3	5

-1 18 L

1	326	214	7
2	165	15Ø	-23
3	78	-79	-2Ø
4	132	118	22
5	71	44	13

-1 19 L

1	149	19	-11
2	196	-83	1Ø
3	43	5	6
4	26	-14	6

-1 2Ø L

1	174	-168	-1
2	147	-97	3
3	7Ø	-54	-13
4	25	13	8

-1 21 L

1	74	9	-4
2	61	35	19
3	72	55	18
4	23	19	Ø

-1 22 L

1	82	59	-4
2	56	-1Ø	-1
3	1Ø3	95	21
4	61	-43	-4

-1 23 L

1	72	-72	Ø
2	83	-66	23
3	98	78	9
4	44	42	Ø

-1 24 L

1	11Ø	22	4
2	65	-63	-1Ø

```
3    16     9     3
                        Ø   416 -378    Ø
   -1   25   L          1   517  519  -22
                        2   246    6    2
1    28   -1Ø  -18      3   367  127   12
2    4Ø   -23   17      4   245 -145   15
3    5Ø    11   -1      5    55  -51   -8
                        6    35    1    5
   -1   26   L
                           Ø   5   L
1    54     6    7
2    56    54    1      1   751 -747  -53
3    34    31    2      2   18Ø   55   -4
                        3   335  33Ø  -19
   -1   27   L          4    69   59   13
                        5    49  -18   -6
1    6Ø    47   13      6    97   85   14
2   -2Ø    16  -13
                           Ø   6   L
   -1   28   L
                        Ø   616  299  -38
1   1Ø8   -99   1Ø      1   395 -259  -17
2    66   -52   1Ø      2   376 -236   13
                        3   121  12Ø   -2
   Ø   Ø   L            4    57   -2   -6
                        5    47   14    6
1   275  291  -68       6    2Ø  -11   -5
2   177 -173   18
3     5   19  -1Ø          Ø   7   L
4   198  198    3
5   -16   -6   -7      1   4Ø2  358  -25
6    57  -61   -8      2   1Ø6   89   21
                        3   153 -133    6
   Ø   1   L            4   133 -121   -7
                        5    48   -5   15
1   4Ø3  157   -8       6    56   34   21
2   217 -141  -37
3   285  -62   28          Ø   8   L
4    96   27    8
5    42   28   -6      Ø   548 -211    Ø
6    29    9   -3      1   3Ø5  -15  -17
                        2   319  314  -2Ø
   Ø   2   L            3    91   -4   37
                        4    64   6Ø   11
Ø   124  1Ø6   54       5    54   42   19
1   83Ø -827  -62       6    42   28   -5
2   441 -372    5
3    32   36  -12          Ø   9   L
4    71   72   -2
5    12   -2   -7      1   173  -91   5Ø
6    37   -4   11      2   135    3   28
                        3   29Ø  -34    Ø
   Ø   3   L            4    57  -54    8
                        5    79   72   16
1   691 -6Ø4  -32       6    34   21    5
2   155 -129   56
3   233  191    5          Ø  1Ø   L
4    43   11   -6
5    78  -77    3      Ø   958 -961   -5
6    53  -12   18      1   198  -57  -2Ø
                        2   247  -55   -9
   Ø   4   L            3   258 -234   32

4    57  -41   37
5    78   -2   -8
6    33   16   -8

   Ø  11   L

1   294 -273   21
2   157  119  -32
3   152  155  -21
4    95  -86  -13
5    4Ø  -29   -6

   Ø  12   L

Ø    76   92  -72
1   33Ø  3Ø9   -2
2    57  -54  -19
3    71   54   -7
4    82   73   31
5    33   25   13

   Ø  13   L

1   144   61   23
2   1Ø3  -1Ø   21
3   188   -3   27
4    47  -23    Ø
5    39    2   -4

   Ø  14   L

Ø   294 -262  -29
1   142  -73   -3
2   143   51    Ø
3   18Ø -1Ø8    5
4    21  -14    7
5    39    6  -19

   Ø  15   L

1   123  -28    Ø
2    93    5    1
3    4Ø  -28    7
4    36  -31   1Ø
5    26  -17    9

   Ø  16   L

Ø   2Ø3  -87   16
1   111  1ØØ   28
2   274  274   -1
3   118 -116   -1
4    61  -58   -5
5    4Ø   -5   1Ø

   Ø  17   L

1   256 -165  -1Ø
2    56  -28   -1
3   162  161    Ø
4    64   61    2
5    13   -8   -2

   Ø  18   L

Ø    71  -48  -1Ø
1     3   26  -21
2   1Ø8   43   3Ø
3    91   15    7
4    24  -26  -17
5    35  -1Ø    7

   Ø  19   L

1   122   95   -4
2   1ØØ  -99    Ø
3    65  -57   11
4    22   18   -2

   Ø  2Ø   L

Ø   187  -58  -23
1   112  111  -32
2   134  111   -8
3    38   28   11
4   113  -53    9

   Ø  21   L

1   137  13Ø   -3
2   1Ø2  -42   -7
3   116 -111   19
4    64   59  -16

   Ø  22   L

Ø   263 -253  -35
1   159 -16Ø   -6
2    75   15    2
3    63  -39    5
4    48  -25    4

   Ø  23   L

1    53   49  -21
2    -5   17  -1Ø
3    22   -8   -9
4    36   33    1

   Ø  24   L

Ø   28Ø  261   29
1    66   67   -3
2    42  -19    7
3    26   26    Ø

   Ø  25   L

1   132   59   15
2    45  -44    2
3    27  -23   -9

   Ø  26   L

Ø    48  -54  -11
1    5Ø  -52   -7
2   11Ø -1Ø3   22
3    61   41   18

   Ø  27   L

1    64  -21    3
2    13  -17   -5

   Ø  28   L

Ø    27    7   -7
1    24   22    1
2    35  -12   16

   1   Ø   L

Ø    84  -9Ø  -34
1   2Ø2  199    8
2    92  1Ø1  -3Ø
3   231  225   15
4    82   81    3
5    95  -94    1
6   -14   14   -6

   1   1   L

Ø   3Ø2  287  -57
1   428 -229   -8
2   395 -382  -47
3   337 -315   -8
4    85  -84   -1
5    9Ø  -75   15
6    5Ø  -46    3

   1   2   L

Ø   4Ø4  289   34
1   551  362  -11
2   167  -53  -13
3   18Ø -176   -4
4    76   7Ø   1Ø
5    19    6    3
6   -23  -19  -17

   1   3   L

Ø   159  -52   -8
1   379  184  -28
2   352  187  -18
3   135   42    7
4    87   77    2
5    78   7Ø   15
6    53   47    9

   1   4   L

Ø   434 -229  -13
1   28Ø  -6Ø    5
2   125  -23   21
3   2Ø5 -119   -8

4   139  121  -14
5    48   48   -5
6    52  -43    Ø

   1   5   L

Ø   458 -31Ø   -7
1   157  154  -37
2   231  2Ø1   19
3    82   64   12
4    92  -95  -18
5    37   -9   -3
6    64   57    5

   1   6   L

Ø   726  7Ø1  -25
1   3Ø1  -71  -3Ø
2   271 -245   11
3    41  -24    6
4    29   35  -11
5    57  -5Ø   -3
6    33  -16   13

   1   7   L

Ø   512  5Ø6    7
1   2ØØ -15Ø   2Ø
2   194 -117   19
3   162  138  -12
4   1Ø6   8Ø   13
5    47  -39   13
6   -25    5  -12

   1   8   L

Ø   4Ø9 -331   -1
1   431  -49    8
2   52Ø   -7   -7
3   154    6   1Ø
4   152  1ØØ  -33
5    73   31   -3
6   -24   -4  -15

   1   9   L

Ø   246  133   1Ø
1   692 -485   15
2   268 -148  -25
3    84   82  -18
4    64  -35  -3Ø
5   117  -88    6
6    32  -18    6

   1  1Ø   L

Ø   386 -237    Ø
1   261  -63   26
2   166  11Ø    Ø
3    6Ø  -53   -9
4   118 -122  -21
5    47   -7  -12
```

6	18	Ø	-6

1 11 L

Ø	222	2Ø5	44
1	2Ø8	-65	-23
2	173	137	-9
3	213	2Ø7	2
4	69	-65	8
5	35	-2Ø	-8

1 12 L

Ø	228	-172	-3
1	352	-344	6
2	126	96	-7
3	223	217	14
4	148	-146	8
5	43	-31	13

1 13 L

Ø	159	-34	-8
1	348	26	9
2	237	-115	21
3	8Ø	-27	-6
4	122	-116	18
5	79	-3Ø	34

1 14 L

Ø	153	-53	-5
1	1Ø5	1Ø	1
2	139	133	-4
3	166	89	8
4	1Ø6	-1Ø2	-3
5	12	-11	Ø

1 15 L

Ø	1Ø3	57	28
1	137	115	1Ø
2	12Ø	19	13
3	46	-29	-5
4	39	-29	4
5	56	46	15

1 16 L

Ø	219	-161	-2
1	82	3Ø	7
2	214	26	23
3	66	-41	23
4	88	-5	11
5	58	46	18

1 17 L

Ø	162	-129	-14
1	78	64	-4
2	125	126	-4
3	71	-63	13
4	31	-31	Ø
5	27	3Ø	-5

1 18 L

Ø	252	255	-19
1	49	16	1Ø
2	59	-15	Ø
3	73	3Ø	5
4	55	-36	-9
5	-11	-1	-2

1 19 L

Ø	29	-1Ø	-18
1	54	35	2Ø
2	33	21	4
3	77	-54	-8
4	84	72	2Ø

1 2Ø L

Ø	35	-42	-22
1	53	-41	-15
2	-25	-2	-18
3	69	67	-6
4	61	21	-4

1 21 L

Ø	1ØØ	-89	-6
1	125	-5Ø	-31
2	75	-7Ø	4
3	8Ø	-75	8
4	36	31	4

1 22 L

Ø	84	-48	-1Ø
1	26	45	-51
2	67	-56	8
3	91	-82	-11
4	-14	14	-8

1 23 L

Ø	85	-47	-3Ø
1	118	113	8
2	127	116	4
3	85	61	4
4	52	38	16

1 24 L

Ø	62	-64	-14
1	38	-11	-12
2	52	42	11
3	45	17	5

1 25 L

Ø	5Ø	-5Ø	-24
1	55	-5	5
2	53	-45	-2
3	54	-46	8

1 26 L

Ø	113	8Ø	-3
1	7	-3	Ø
2	16	2Ø	-4
3	22	-19	-7

1 27 L

Ø	21	-24	-16
1	31	22	8
2	26	-11	-9

1 28 L

Ø	3Ø	-4Ø	-15
1	13	-1	-9
2	32	-24	-1

2 Ø L

Ø	241	221	63
1	1Ø6Ø	1Ø99	-37
2	383	-389	-13
3	333	-336	-6
4	45	-47	-2
5	1ØØ	1Ø5	-13
6	33	-3	15

2 1 L

Ø	452	338	18
1	981	-736	-15
2	144	21	-9
3	167	97	-4
4	45	19	11
5	72	-64	-7
6	2	-3	-7

2 2 L

Ø	276	9	Ø
1	1158	12Ø7	-62
2	18Ø	-79	37
3	83	-66	28
4	219	118	12
5	31	32	-6
6	-28	-2Ø	-24

2 3 L

Ø	357	21Ø	-5
1	1246	-1Ø44	-43
2	345	-341	-8
3	81	-48	17
4	96	1Ø8	-4Ø
5	71	-58	2Ø
6	13	-23	-7

2 4 L

Ø	558	-532	21
1	269	238	-28
2	111	-67	-42
3	223	-97	4
4	48	52	-28
5	55	-32	12
6	2Ø	-12	-8

2 5 L

Ø	652	563	-11
1	445	395	-47
2	233	28	14
3	99	87	14
4	171	168	8
5	64	61	7
6	39	-5	21

2 6 L

Ø	265	-256	2
1	187	-92	55
2	371	351	1Ø
3	61	46	2Ø
4	1Ø6	-89	-1Ø
5	8Ø	-9	-27
6	48	39	9

2 7 L

Ø	66	41	3Ø
1	475	-249	-5
2	232	-2Ø7	4
3	113	-31	-4
4	135	-138	-19
5	42	-22	8
6	35	18	11

2 8 L

Ø	43	36	16
1	536	-481	24
2	196	-18Ø	15
3	2Ø	-15	-4
4	44	-34	17
5	48	-41	12
6	23	11	6

2 9 L

Ø	244	83	-9
1	184	-66	-28
2	68	-1	-13
3	57	49	-17
4	1Ø7	36	6
5	22	-14	-8

2 1Ø L

Ø	29Ø	213	-4
1	1ØØ	-8Ø	29
2	245	87	-1Ø
3	113	113	Ø
4	155	12Ø	9
5	38	28	7

2 11 L

Ø	273	139	24
1	387	315	34
2	28	-4	6
3	99	-1Ø9	-38
4	14	31	-19
5	33	-24	8

2 12 L

Ø	64	-28	12
1	385	-376	25
2	87	-83	Ø
3	148	-147	-7
4	191	-143	-14
5	28	6	5

2 13 L

Ø	225	111	21
1	53	-48	1Ø
2	9Ø	-48	18
3	147	117	-17
4	126	-3	5
5	27	-29	-2

2 14 L

Ø	367	29Ø	8
1	-4	-4	-8
2	2Ø5	1Ø4	19
3	218	226	-29
4	39	33	4
5	36	2	5

2 15 L

Ø	237	29	32
1	168	-54	-5
2	87	-9Ø	-12
3	52	38	12
4	5Ø	1Ø	-6
5	32	-2Ø	Ø

2 16 L

Ø	161	125	-1
1	2Ø6	-19Ø	5
2	152	-137	-14
3	27	19	4
4	42	-17	-11
5	15	-17	-1

2 17 L

Ø	153	74	-13
1	123	12Ø	-1
2	1Ø7	43	-6
3	23	Ø	11
4	1Ø6	8Ø	26
5	19	5	6

2 18 L

Ø	99	-27	21
1	69	-18	2
2	18Ø	179	3
3	76	75	-3
4	52	-52	Ø

2 19 L

Ø	187	-167	5
1	253	-187	Ø
2	113	-14	24
3	61	-26	6
4	44	-46	-9

2 2Ø L

Ø	81	-86	-33
1	1Ø6	-1Ø6	-25
2	32	2	-21
3	142	59	-3
4	81	-5Ø	9

2 21 L

Ø	61	-62	-14
1	81	Ø	-4
2	83	75	1
3	3Ø	-16	4
4	28	-27	-13

2 22 L

Ø	98	-16	18
1	61	-8	-7
2	35	11	6
3	42	4Ø	-12
4	22	29	-8

2 23 L

Ø	63	-6Ø	3
1	1Ø9	97	7
2	9Ø	37	-3
3	74	-79	-13

2 24 L

Ø	43	27	-15
1	-25	5	-14
2	22	-24	-18
3	88	-8Ø	18

2 25 L

Ø	129	-29	29
1	7Ø	12	3
2	57	41	-4
3	18	1	4

2 26 L

Ø	87	-11	8
1	2Ø	34	-13
2	39	-26	15

2 27 L

Ø	29	-4	-5
1	1Ø1	-79	8
2	73	-46	2Ø

2 28 L

Ø	36	-38	-2
1	-14	13	-7

3 Ø L

Ø	385	-367	38
1	3Ø2	3Ø2	Ø
2	169	168	3
3	7	29	-14
4	77	-81	-1Ø
5	51	56	-7
6	38	Ø	19

3 1 L

Ø	56Ø	-549	4
1	84	3	23
2	1ØØ	88	-4
3	71	-4Ø	27
4	84	-72	-5
5	-17	18	-15
6	31	23	5

3 2 L

Ø	535	-478	-14
1	389	-286	-19
2	361	114	-1Ø
3	198	-1	-5
4	8Ø	-73	3
5	27	17	6
6	24	2	Ø

3 3 L

Ø	454	-351	35
1	156	36	17
2	41	-32	11
3	127	-74	6
4	7Ø	-6Ø	2
5	64	17	-12
6	23	1Ø	3

3 4 L

Ø	5ØØ	251	8
1	319	31Ø	26
2	384	313	8
3	142	96	-5
4	48	36	3
5	57	3Ø	7
6	9	9	-2

3 5 L

Ø	429	255	7
1	316	222	16
2	86	5	9
3	67	2Ø	6
4	125	88	8
5	21	13	-12
6	3Ø	-14	5

3 6 L

Ø	52Ø	-214	4
1	1Ø9	-1Ø	16
2	557	-483	-1Ø
3	27Ø	-249	-3
4	2Ø	-11	4
5	57	6Ø	-11
6	37	-12	Ø

3 7 L

Ø	482	-295	11
1	61	52	25
2	252	-4	26
3	55	-37	8
4	84	38	29
5	8	-13	-6

3 8 L

Ø	384	391	-23
1	26Ø	23Ø	15
2	296	54	-9
3	44	25	5
4	29	1Ø	1Ø
5	38	-4	Ø

3 9 L

Ø	184	39	-4Ø
1	119	-5Ø	21
2	237	-22Ø	2
3	32	4	11
4	1Ø1	83	16
5	34	-35	-13

3 1Ø L

Ø	252	-152	32
1	433	-418	1
2	78	-76	-12
3	2Ø9	42	2
4	47	41	-2Ø
5	74	-59	31

3 11 L

Ø	285	241	-2
1	172	139	-19
2	11Ø	-59	7
3	89	76	13
4	1Ø9	11Ø	-14
5	85	-88	-15

3 12 L

Ø	35Ø	329	4
1	146	8Ø	17
2	1Ø9	-17	19
3	93	46	1
4	49	49	Ø
5	67	-68	-5

3 13 L

Ø	277	-259	9
1	147	72	22
2	69	34	-5
3	98	-1Ø2	-15
4	36	-19	-2
5	31	-2	12

3 14 L

Ø	17Ø	-167	-15
1	254	-251	1Ø
2	87	-71	-3
3	131	35	16
4	36	-21	-8
5	63	-43	33

3 15 L

Ø	169	-74	3
1	171	71	-1
2	186	156	16
3	54	55	-4
4	78	-54	14
5	38	-19	3

3 16 L

Ø	221	17Ø	5
1	198	149	2
2	1Ø6	1Ø6	Ø
3	124	115	2
4	49	38	-18
5	35	21	-5

3 17 L

Ø	37	-36	Ø
Ø	66	66	Ø
1	124	-35	-2Ø
2	68	-31	-33
3	48	13	-3
4	28	-17	3

3 18 L

Ø	127	-29	Ø
1	16	-17	-6
2	2Ø2	-2Ø2	-9
3	1Ø6	-1Ø4	7
4	15	-4	Ø

3 19 L

Ø	179	-1ØØ	Ø
1	7Ø	-7Ø	-3
2	34	13	-4
3	97	-28	-17
4	1Ø1	-18	12

3 2Ø L

Ø	181	122	-7
1	6Ø	49	8
2	99	95	1Ø
3	13	26	-17
4	15	17	-7

3 21 L

Ø	56	36	4
1	144	-11Ø	13
2	53	16	4
3	4Ø	51	-18
4	24	-17	5

3 22 L

Ø	1Ø5	-5	23
1	132	-126	1
2	26	7	-1
3	-16	7	-11

3 23 L

Ø	122	122	-12
1	86	-6Ø	2
2	53	-36	-8
3	43	42	1

3 24 L

Ø	41	-1	5
1	57	39	2Ø
2	96	-5	-2Ø
3	3Ø	-2	15

3 25 L

Ø	37	-36	Ø
1	78	-1	Ø
2	48	5Ø	-5
3	32	6	18

3 26 L

Ø	1Ø4	-86	36
1	31	-34	-4
2	34	Ø	2Ø

3 27 L

Ø	74	-53	-18
1	24	-36	-14
2	35	32	2

3 28 L

Ø	35	14	3
1	56	34	-4

4 Ø L

Ø	437	-422	3Ø
1	33Ø	-327	7
2	155	-149	2Ø
3	131	-131	1
4	19	6	6
5	16	44	-26

4 1 L

Ø	2Ø8	-198	45
1	427	-231	53
2	3Ø2	-26Ø	21
3	55	-3	-12
4	77	49	-11
5	57	46	-4

4 2 L

Ø	419	337	26
1	325	31Ø	3Ø
2	637	458	1Ø
3	98	-83	-11
4	114	-113	-5
5	46	19	24

4 3 L

Ø	218	183	61
1	15Ø	72	-33
2	345	-34Ø	9
3	61	65	-13
4	66	66	-7
5	42	32	3

4 4 L

Ø	391	-375	46
1	374	-354	38
2	4Ø2	364	-37
3	66	59	-9
4	13	-16	-23
5	37	36	Ø

4 5 L

Ø	441	-248	17
1	148	114	34
2	33Ø	-324	-3
3	92	-62	-26
4	58	-25	-7
5	56	-3Ø	24

4 6 L

Ø	122	-57	-8
1	245	-21Ø	-21
2	212	-8	27
3	2Ø1	78	-24
4	21	-13	4
5	113	-85	3

4 7 L

Ø	158	-13	-36
1	287	286	3
2	138	-13	2
3	42	-38	-6
4	91	54	-12
5	78	61	18

4 8 L

Ø	351	-3Ø3	52
1	1Ø8	-1ØØ	12
2	36Ø	-159	17
3	123	19	-2Ø
4	63	-15	Ø
5	38	-8	12

4 9 L

Ø	224	-2ØØ	-12
1	2Ø3	74	-16
2	94	65	3Ø
3	129	-87	-11
4	72	-71	-3
5	48	-32	-5

4 1Ø L

Ø	258	187	3
1	416	245	11
2	92	-22	-16
3	-12	13	-24
4	3Ø	14	3
5	119	53	1

4 11 L

Ø	3Ø5	-124	32
1	128	117	2Ø

2	197	114	0
3	75	4	5
4	32	12	8
5	17	0	-5

4 12 L

0	64	-61	8
1	46	50	-10
2	190	-179	11
3	47	-52	-21
4	40	24	15
5	54	-11	14

4 13 L

0	177	-8	5
1	173	100	6
2	113	10	-4
3	126	-40	12
4	34	33	-13
5	52	0	-16

4 14 L

0	227	218	12
1	338	215	-1
2	159	-120	-33
3	80	-47	-7
4	74	51	10
5	23	0	-16

4 15 L

0	250	246	9
1	95	67	14
2	65	25	-40
3	-16	1	-7
4	81	49	7
5	8	22	-10

4 16 L

0	111	88	-9
1	65	57	14
2	127	-41	-18
3	88	28	4
4	82	59	-6

4 17 L

0	79	62	-12
1	153	-152	3
2	67	-62	5
3	22	0	11
4	51	-6	1

4 18 L

0	169	165	-12
1	46	-44	-2
2	107	-94	11
3	21	16	-10
4	45	4	-7

4 19 L

0	17	10	-1
1	64	-62	-4
2	54	-30	11
3	56	52	-12
4	49	12	3

4 20 L

0	70	-65	10
1	91	-96	-17
2	65	-42	-5
3	57	49	4
4	26	17	2

4 21 L

0	53	-32	20
1	80	-29	-1
2	-11	-10	-7
3	34	-2	9
4	61	-58	0

4 22 L

0	57	55	-10
1	104	99	0
2	110	100	12
3	47	20	-5

4 23 L

0	58	34	10
1	3	-10	-7
2	57	44	10
3	43	0	1

4 24 L

0	82	-69	7
1	87	-82	7
2	86	-74	11
3	45	-46	-3

4 25 L

0	37	-33	-8
1	22	-29	-7
2	26	-3	13

4 26 L

0	24	32	-11
1	42	32	0
2	43	-4	12

4 27 L

0	59	46	9
1	23	22	-3

4 28 L

0	58	-55	4
1	55	-20	3

5 0 L

0	109	-112	-9
1	401	-415	-31
2	89	-87	4
3	54	38	21
4	189	-186	7
5	84	-83	1

5 1 L

0	751	-82	52
1	62	55	8
2	197	97	16
3	247	245	5
4	124	71	19
5	42	-11	9

5 2 L

0	157	-35	-14
1	228	-186	54
2	109	98	11
3	212	174	-17
4	144	121	-31
5	9	3	1

5 3 L

0	436	-330	26
1	149	-62	12
2	93	-1	-5
3	105	-80	24
4	97	-93	7
5	24	-13	-6

5 4 L

0	263	230	47
1	598	62	11
2	117	-4	5
3	291	-104	-5
4	51	14	-23
5	33	-19	-20

5 5 L

0	180	-121	35
1	75	-58	22
2	163	161	3
3	155	-157	-13
4	75	-48	-1
5	62	68	-14

5 6 L

0	339	-211	42
1	187	53	-11
2	99	78	12
3	64	6	-6
4	77	-68	8
5	53	34	-14

5 7 L

0	142	-77	1
1	129	-127	3
2	27	1	1
3	112	86	-8
4	37	19	13
5	25	-11	0

5 8 L

0	214	-22	20
1	193	64	9
2	174	-142	8
3	117	-105	0
4	50	-23	-5
5	67	37	18

5 9 L

0	460	267	12
1	73	75	-11
2	112	-97	6
3	84	21	-26
4	97	43	13
5	44	34	-3

5 10 L

0	144	106	11
1	242	170	-8
2	137	34	17
3	30	-10	3
4	73	47	20
5	21	6	5

5 11 L

0	177	-175	8
1	144	-143	2
2	61	-2	-6
3	114	-89	23
4	30	3	-13
5	45	36	10

5 12 L

0	87	-65	29
1	146	-122	29
2	31	-22	-1
3	40	24	15
4	19	-19	-2
5	64	-30	11

5 13 L

0	244	215	2
1	21	7	9
2	152	151	-17
3	82	80	-10
4	80	16	17
5	-4	-17	-6

5 14 L

0	136	19	13
1	46	27	9
2	102	-6	8
3	40	43	-1
4	52	36	-4

5 15 L

0	166	-33	23
1	80	-92	-17
2	51	22	13
3	-14	21	-16
4	38	-20	3

5 16 L

0	177	147	5
1	162	119	17
2	32	-31	-3
3	98	-75	4
4	7	-2	-3

5 17 L

0	169	-108	-6
1	57	59	-3
2	56	12	0
3	46	-32	2
4	35	-11	9

5 18 L

0	187	-57	2
1	-18	21	-25
2	51	28	12
3	39	-28	-30
4	-8	-3	-8

5 19 L

0	90	-59	4
1	50	28	-6
2	112	-85	34
3	34	7	2
4	23	3	8

5 20 L

0	24	-10	4
1	181	58	2
2	48	-41	-7
3	89	-38	-1

5 21 L

0	169	149	17
1	28	27	-16
2	82	-65	5
3	32	26	-8

5 22 L

0	47	31	10
1	80	70	-4
2	27	-7	12
3	68	51	2

5 23 L

0	34	-17	-3
1	13	-12	0
2	53	-51	-4
3	63	-49	19

5 24 L

0	47	-22	18
1	99	-76	6
2	50	-51	-9

5 25 L

0	92	-20	8
1	41	17	10
2	67	17	-8

5 26 L

0	81	-71	24
1	73	-55	11

5 27 L

0	-14	11	-6
1	10	-16	-3

6 0 L

0	143	123	55
1	222	223	0
2	119	115	9
3	150	-159	-25
4	18	27	-6
5	15	13	0

6 1 L

0	122	113	8
1	88	-86	-13
2	106	43	0
3	51	32	3
4	43	-44	-11

5	-12	7	-8

6 2 L

Ø	1Ø2	73	1
1	187	-172	16
2	155	-131	1Ø
3	96	22	14
4	35	-3Ø	6
5	33	-25	7

6 3 L

Ø	21Ø	84	18
1	128	-97	1Ø
2	77	-37	6
3	242	-16	-31
4	7Ø	62	1Ø
5	28	25	Ø

6 4 L

Ø	39Ø	223	-6
1	55	42	1Ø
2	15	-11	-4
3	292	283	-2
4	23	-2	-1Ø
5	19	-11	-8

6 5 L

Ø	124	-1Ø5	21
1	186	-114	-2Ø
2	19Ø	-183	1Ø
3	282	-288	-21
4	83	64	-18
5	-16	11	-18

6 6 L

Ø	392	-345	3Ø
1	152	-144	22
2	234	-12Ø	-2
3	61	-48	27
4	71	-19	-19
5	26	-8	11

6 7 L

Ø	1Ø7	-35	-2
1	85	-63	-5
2	3Ø6	261	-13
3	45	-42	-16
4	54	-49	6
5	34	-2Ø	13

6 8 L

Ø	42Ø	112	19
1	129	-66	19
2	167	122	1Ø
3	99	94	13
4	1Ø6	73	-19
5	56	-37	11

6 9 L

Ø	291	-173	-1
1	1Ø4	-1ØØ	8
2	186	185	Ø
3	1Ø9	1Ø5	1Ø
4	66	-52	13
5	11	2	-2

6 1Ø L

Ø	63	13	-3
1	317	-186	4
2	129	-126	-14
3	89	-61	-13
4	28	-27	-3
5	5Ø	Ø	2

6 11 L

Ø	1Ø4	-91	9
1	12Ø	-22	Ø
2	71	-74	-16
3	79	-45	9
4	41	-11	-3
5	38	33	5

6 12 L

Ø	238	-216	13
1	353	346	18
2	223	221	-7
3	38	-41	-5
4	45	-27	5

6 13 L

Ø	94	-9	6
1	151	145	2Ø
2	199	189	-14
3	1Ø9	51	-16
4	4Ø	-14	4

6 14 L

Ø	271	-147	9
1	173	21	-2Ø
2	3Ø	7	2Ø
3	111	-11Ø	-11
4	23	-19	-2

6 15 L

Ø	1Ø1	1Ø2	-7
1	51	38	-13
2	67	-66	1
3	12	-2	-2
4	32	1Ø	3

6 16 L

Ø	215	199	4Ø
1	7Ø	42	9
2	54	19	-18
3	57	-27	6
4	49	46	4

6 17 L

Ø	152	6Ø	-9
1	136	53	3
2	178	-14Ø	-6
3	35	-35	Ø
4	36	28	-5

6 18 L

Ø	143	-116	Ø
1	53	-18	12
2	63	-56	-2
3	75	-65	3
4	18	-6	3

6 19 L

Ø	179	11	-18
1	28	3	-3
2	31	27	4
3	62	22	-1

6 2Ø L

Ø	9Ø	-12	2Ø
1	66	53	21
2	92	54	16
3	82	76	5

6 21 L

Ø	52	-42	-3
1	44	-46	-6
2	45	-8	4
3	29	8	-8

6 22 L

Ø	94	56	-4
1	52	-5Ø	-5
2	38	-28	Ø
3	45	-21	-5

6 23 L

Ø	49	-26	6
1	45	32	15
2	-22	-6	-13

6 24 L

Ø	35	-4	-7
1	17	25	-8
2	28	25	-9

6 25 L

Ø	34	18	2
1	16	6	1

6 26 L

Ø	25	-21	-2
1	43	8	19

7 Ø L

Ø	16	21	-3
1	73	65	16
2	19Ø	-185	13
3	19	-21	-1
4	34	52	-22
5	9	23	-5

7 1 L

Ø	117	-111	18
1	239	-7	3
2	1Ø7	1Ø4	2
3	7Ø	-12	9
4	66	-39	-3
5	38	-15	8

7 2 L

Ø	186	176	19
1	111	-37	2
2	16Ø	-65	14
3	86	66	11
4	2Ø	11	5
5	31	-13	5

7 3 L

Ø	183	44	68
1	21	-15	4
2	138	115	7
3	44	33	8
4	18	4	5
5	11	-13	-1

7 4 L

Ø	26	-13	13
1	148	-14Ø	2Ø
2	128	-27	-1
3	-16	-2	-7
4	136	-24	5
5	14	-16	-5

7 5 L

Ø	178	-94	11
1	25Ø	-239	26
2	193	-158	2
3	39	-11	-13
4	37	-24	16
5	39	-23	16

7 6 L

Ø	269	187	Ø
1	32Ø	3Ø4	17
2	1Ø5	1Ø6	-11
3	72	-62	-13
4	67	21	-1
5	45	31	12

7 7 L

Ø	17Ø	133	19
1	172	165	2
2	76	18	13
3	31	1	1Ø
4	52	-36	-11
5	14	19	-9

7 8 L

Ø	14Ø	-112	11
1	76	-74	-1
2	116	-61	8
3	62	-49	3
4	42	-23	6
5	28	9	9

7 9 L

Ø	34	11	-4
1	156	33	-32
2	113	-5Ø	1Ø
3	43	-34	6
4	56	45	-4

7 1Ø L

Ø	154	152	-24
1	293	18	-1
2	99	9Ø	11
3	59	6Ø	Ø
4	1Ø	-29	-16

7 11 L

Ø	168	139	14
1	16	13	-2
2	98	-1ØØ	-5
3	-17	5	-8
4	73	71	4

7 12 L

Ø	18Ø	-129	-4
1	125	-126	-14
2	75	-63	1Ø
3	28	-8	-6
4	75	55	23

7 13 L

Ø	246	-43	-1Ø
1	89	56	2
2	44	-36	3
3	36	39	-4
4	52	-43	3

7 14 L

Ø	146	62	2
1	22Ø	138	16
2	87	9Ø	-6
3	4Ø	4Ø	-1
4	34	-15	12

7 15 L

Ø	174	-1Ø8	-14
1	154	43	1Ø
2	116	77	8
3	51	59	-22
4	34	-3Ø	-2

7 16 L

Ø	243	-241	9
1	2Ø1	-195	-14
2	49	-49	-1
3	6Ø	-15	9
4	38	-43	-9

7 17 L

Ø	44	-46	-29
1	162	-132	1
2	58	-13	-1
3	59	-44	17

7 18 L

Ø	147	-34	15
1	138	1Ø7	1Ø
2	13Ø	121	3
3	49	-27	8

7 19 L

Ø	1Ø9	1Ø1	18
1	63	24	22
2	76	56	3
3	35	-33	Ø

7 2Ø L

Ø	64	-75	-29
1	66	5Ø	-1Ø
2	1Ø6	21	-2
3	47	-5Ø	-6

7 21 L

Ø	57	-33	9
1	-28	1Ø	-19
2	-17	9	-13

7 22 L

Ø	59	2	7
1	51	-47	-2
2	67	-37	15

7 23 L

Ø	84	56	11
1	19	-8	4
2	48	-52	-6

7 24 L

Ø	54	34	8
1	14	-11	-9

7 25 L

Ø	29	-2Ø	Ø
1	63	-35	2

8 Ø L

Ø	1Ø3	1Ø9	-14
1	227	233	-16
2	-7	4	-1
3	35	-41	-6
4	-24	11	-1Ø

8 1 L

Ø	283	274	11
1	25Ø	216	-31
2	47	-14	-1Ø
3	38	-32	-16
4	36	19	12

8 2 L

Ø	278	-1Ø4	16
1	54	12	11
2	95	-17	1
3	92	-43	1
4	61	-26	4

8 3 L

Ø	185	65	-1
1	116	-6Ø	-1
2	147	-117	Ø
3	46	-35	-9
4	66	5	-6

8 4 L

Ø	37	-3Ø	3
1	65	-3Ø	7
2	58	-36	-16
3	54	-4	-23
4	47	-35	-1

8 5 L

Ø	333	335	-6
1	14Ø	-38	-17
2	47	-45	5
3	29	-3	17
4	44	-43	Ø

8 6 L

Ø	171	137	5
1	73	2	-6
2	64	-36	17
3	89	72	-18
4	128	11Ø	13

8 7 L

Ø	214	-47	3
1	1ØØ	-14	2
2	113	-84	7
3	7Ø	-25	6
4	59	-58	-5

8 8 L

Ø	2Ø6	2Ø4	-6
1	129	-98	-5
2	9Ø	-33	1
3	95	-39	-1
4	21	35	-15

8 9 L

Ø	161	45	-3
1	2Ø8	62	-4
2	63	42	28
3	12Ø	119	-1
4	23	-6	-1Ø

8 1Ø L

Ø	239	-186	-3
1	138	-135	-12
2	47	35	6
3	51	35	7
4	43	-4	15

8 11 L

Ø	85	-37	-8
1	177	-158	8
2	36	29	-1
3	68	62	-2
4	33	-28	5

8 12 L

Ø	2Ø	17	-6
1	192	149	-25
2	72	65	15
3	42	17	16
4	39	-42	-5

8 13 L

Ø	81	-5Ø	-28
1	112	59	21
2	117	1ØØ	13
3	-12	-11	-6
4	35	25	1Ø

8 14 L

Ø	128	-72	-8
1	157	-44	Ø
2	35	43	-18
3	63	-1Ø	22

8 15 L

Ø	95	-46	-5
1	122	1Ø7	-3
2	3Ø	-2Ø	7
3	73	-66	14

8 16 L

Ø	67	-36	1
1	5Ø	-48	3
2	32	-2	8
3	22	-36	-17

8 17 L

Ø	1ØØ	47	-6
1	59	-15	-23
2	37	-29	-18
3	65	15	8

8 18 L

Ø	21	21	Ø
1	66	37	2
2	64	-39	6
3	4Ø	41	-1

8 19 L

Ø	85	-68	4
1	94	-58	Ø
2	71	15	-1

8 2Ø L

Ø	66	28	5
1	65	-21	-4
2	17	-18	-8

8 21 L

Ø	44	36	7
1	42	27	15
2	-18	16	-12

8 22 L

Ø	89	-73	Ø
1	94	-5Ø	-4

8 23 L

Ø	98	-97	Ø
1	9Ø	-75	2Ø

8 24 L

Ø	62	34	-1

9 Ø L

Ø	94	96	-4
1	128	137	-24
2	84	96	-25
3	61	61	1
4	65	6Ø	7

9 1 L

Ø	66	-18	14
1	74	-49	2
2	58	12	4
3	44	2Ø	1Ø
4	-4	-3	Ø

9 2 L

Ø	86	-88	-6
1	69	-69	-2
2	138	-119	-24
3	93	-78	5
4	63	-32	2

9 3 L

Ø	119	1Ø9	-17
1	54	-24	19
2	155	5	-14
3	34	22	6
4	44	-5	15

9 4 L

Ø	1Ø2	-85	8
1	76	37	-1Ø
2	75	66	1Ø
3	33	12	18
4	8	8	Ø

9 5 L

Ø	15Ø	-119	-8
1	1ØØ	25	-24
2	35	26	1Ø
3	32	21	-4
4	38	-38	-1

9 6 L

Ø	51	-2Ø	7
1	54	45	8
2	95	83	5
3	46	-33	18
4	24	-32	-1Ø

9 7 L

Ø	47	49	-1Ø
1	1Ø4	67	-14
2	37	-8	12
3	41	-29	-4
4	32	-28	2

9 8 L

Ø	144	-56	Ø
1	96	88	-33
2	32	36	-7
3	115	3Ø	24
4	33	Ø	Ø

9 9 L

Ø	8Ø	55	-25
1	21	7	Ø
2	49	14	11
3	76	-72	1
4	31	21	3

9 1Ø L

Ø	1Ø1	-9	-11
1	87	-24	16
2	142	-7Ø	-6
3	7	-22	-11
4	-27	3	-17

9 11 L

Ø	88	29	Ø
1	15Ø	47	5
2	86	83	-7
3	3Ø	-2Ø	-15

9 12 L

Ø	216	214	Ø
1	71	-22	-7
2	61	38	-7
3	18	27	-11

9 13 L

Ø	55	-47	11
1	111	-34	-11
2	89	-37	-8
3	28	6	8

9 14 L

Ø	38	-6	14
1	94	-9Ø	Ø
2	114	-81	-16
3	45	5	14

9 15 L

Ø	52	Ø	-3
1	79	-51	-19
2	23	-11	2
3	26	27	-2

9 16 L

Ø	44	-21	3
1	35	19	Ø
2	47	-31	8
3	66	44	11

9 17 L

Ø	39	-4Ø	-6
1	59	-6Ø	-7
2	48	4Ø	4

9 18 L

Ø	47	6	-5
1	64	-28	8
2	46	23	22

9 19 L

Ø	59	6Ø	-1
1	4Ø	31	5
2	22	-13	-9

9 2Ø L

Ø	27	-6	11
1	71	-15	11
2	55	49	2

9 21 L

Ø	55	-23	-8
1	55	57	-3

9 22 L

Ø	39	-15	-5

1Ø Ø L

Ø	116	-116	-1

1	5	-4	0
2	31	34	-3
3	33	-34	0
4	52	-37	16

10 1 L

0	122	-119	7
1	162	6	-30
2	97	-62	-16
3	53	-2	-3
4	27	20	0

10 2 L

0	65	10	-2
1	111	88	-42
2	74	72	2
3	53	-3	-15
4	27	-5	6

10 3 L

0	96	-59	-8
1	163	148	-34
2	31	-20	12
3	44	-34	4
4	54	-11	12

10 4 L

0	176	-118	-25
1	113	-113	-1
2	137	-76	-13
3	60	-43	9
4	48	-3	-7

10 5 L

0	38	4	3
1	90	88	2
2	15	9	2
3	72	-40	6

10 6 L

0	179	135	-21
1	102	92	-6
2	47	43	7
3	41	36	-3

10 7 L

0	80	-72	11
1	20	13	-16
2	19	5	-3
3	18	4	6

10 8 L

0	38	-1	2
1	45	-46	-10
2	113	-105	-5
3	27	-6	-5

10 9 L

0	145	-147	-8
1	106	-76	-5
2	23	-22	0
3	-30	11	-21

10 10 L

0	28	22	6
1	10	6	0
2	79	0	-18
3	71	58	17

10 11 L

0	40	22	19
1	33	5	18
2	87	83	0
3	77	76	0

10 12 L

0	57	-60	-9
1	22	-19	0
2	111	35	-11
3	26	-2	11

10 13 L

0	80	-55	14
1	97	-83	4
2	37	-5	11
3	-27	-11	-18

10 14 L

0	30	19	9
1	25	12	0
2	31	38	-10

10 15 L

0	38	0	0
1	61	33	21
2	35	24	12

10 16 L

0	61	39	16
1	26	-18	5
2	61	-44	13

10 17 L

0	50	52	-4
1	38	27	-4
2	24	-22	0

10 18 L

0	102	107	-14
1	56	41	9

10 19 L

0	88	60	-9
1	-22	-4	-10

10 20 L

0	46	-38	1

11 0 L

0	120	128	-18
1	43	48	-5
2	-12	-21	-9
3	47	-41	7

11 1 L

0	23	-17	5
1	53	-20	-16
2	51	21	0
3	42	18	-4

11 2 L

0	9	-7	0
1	51	-57	-16
2	29	-12	14
3	40	24	6

11 3 L

0	158	-32	-3
1	81	-82	-5
2	47	-34	10
3	51	19	-2

11 4 L

0	59	-15	12
1	25	-33	-10
2	39	15	-12
3	3	13	-3

11 5 L

0	127	121	4
1	59	52	8
2	48	45	-16
3	42	44	-4

11 6 L

0	81	-81	-15
1	59	-15	4
2	46	28	10
3	45	1	21

11 7 L

0	193	-166	9
1	72	-69	-17
2	43	21	26
3	20	-2	4

11 8 L

0	76	19	-7
1	65	28	-3
2	101	34	-10
3	70	42	4

11 9 L

0	47	11	-20
1	80	74	13
2	44	8	12
3	46	4	-5

11 10 L

0	41	-25	11
1	38	0	3
2	53	-24	-12

11 11 L

0	43	-27	-1
1	17	0	1
2	48	-40	0

11 12 L

0	52	50	1
1	64	65	-1
2	46	5	9

11 13 L

0	120	17	5
1	29	-13	11
2	55	19	-9

11 14 L

0	36	2	25
1	46	-47	-7
2	62	-58	6

11 15 L

0	68	-64	0
1	68	-70	-5

11 16 L

0	69	29	0
1	36	35	0

11 17 L

0	116	103	15
1	48	46	-9

11 18 L

0	64	-61	3

12 0 L

0	104	107	-5
1	66	-72	-10
2	60	47	16

12 1 L

0	76	-81	-31
1	48	-47	-7
2	52	-32	-1

12 2 L

0	59	-9	-3
1	22	-20	1
2	64	16	14

12 3 L

0	108	84	-4
1	28	23	4
2	30	33	-3

12 4 L

0	54	-6	7
1	93	60	9
2	24	6	-3

12 5 L

0	34	36	-6
1	63	-41	-2
2	35	36	-7

12 6 L

0	57	46	-5
1	60	-45	-6
2	66	-65	-16

12 7 L

0	102	91	-18
1	43	-11	3
2	3	-8	-1

12 8 L

0	33	27	-8
1	-16	11	-8
2	37	9	25

12 9 L

0	28	-2	0
1	93	-92	-9
2	43	-41	0

12 10 L

0	64	-31	-3
1	38	25	12
2	18	-9	1

12 11 L

0	22	29	-11
1	66	-47	4

12 12 L

0	59	-61	-13
1	50	-33	14

12 13 L

0	83	-85	-11
1	32	10	0

12 14 L

0	63	-59	7

12 15 L

0	-19	8	-11

13 0 L

0	55	-49	6
1	11	-22	-4

13 1 L

0	69	57	-8
1	58	-46	-1

13 2 L

0	78	59	4
1	95	80	-2

13 3 L

0	73	55	16
1	29	-25	-2

13 4 L

0	91	-4	8
1	31	-17	-1

13 5 L

```
 Ø     61    65   -18
 1    -13    15    -7

    13     6   L

 Ø     87   -5Ø   -12
```

```
 1     83   -59    24

    13     7   L

 Ø     58    36    Ø
 1     22    -6     5
```

```
    13     8   L

 Ø     2Ø   -25    -7
 1     11   -14    -4

    13     9   L
```

```
 Ø     33   -16     4

    13    1Ø   L

 Ø     71    63    14

    13    11   L
```

```
 Ø     3Ø   -16    -1

    14     Ø   L

 Ø     29   -32    -2
```

```
    14     1   L

 Ø    -2Ø    2Ø   -16

    14     2   L

 Ø    -16     Ø    -6
```

Appendix B. Structure factor amplitudes ($10F_o$, $10F_c$, $10\sigma_F$; $\sigma_F/k = [F_o + \sigma_{F^2}]^{\frac{1}{2}} - |F_o|$, $k = 1.9012$; $F_o < 0$ means $I_o < 0$) for *trans*-Os(η^4-CHBA-HMEt)$(py)_2$.

-13 1 L

1	138	-124	1

-13 2 L

1	263	-19Ø	16
2	-2Ø4	-31	-24

-13 3 L

1	264	-23Ø	8
2	77	75	Ø

-13 4 L

1	194	-148	8
2	194	175	3
3	174	123	7

-13 5 L

1	-124	-23	-9
2	33Ø	256	2Ø
3	-177	18	-18

-13 6 L

1	47	83	-2
2	289	25Ø	1Ø

-13 7 L

1	2Ø7	169	7
2	218	169	9

-13 8 L

1	13Ø	192	-1Ø

-12 Ø L

1	319	-176	36
2	-15Ø	79	-17
3	284	178	25
4	-148	-114	-2Ø
5	2Ø5	-159	8

-12 1 L

1	-43	-83	-5
2	172	146	4
3	-1Ø4	126	-15
4	242	-225	4
5	-115	1	-7

-12 2 L

1	-146	-29	-14
2	289	235	15
3	-167	-15	-17
4	259	-18Ø	18
5	-185	44	-21
6	-1Ø2	1Ø5	-11

-12 3 L

1	-219	71	-35
2	19Ø	2ØØ	-2
3	-161	-62	-18
4	17Ø	-171	Ø
5	-128	29	-1Ø
6	158	127	4

-12 4 L

1	222	18Ø	9
2	132	168	-6
3	129	-198	-13
4	151	-13Ø	3
5	115	115	Ø
6	-82	66	-6

-12 5 L

1	25Ø	279	-8
2	-52	53	-3
3	333	-271	18
4	-167	-5Ø	-18
5	272	185	2Ø
6	-19Ø	23	-21

-12 6 L

1	354	353	Ø
2	-175	-61	-22
3	349	-278	22
4	-12Ø	64	-11
5	227	2Ø4	5

-12 7 L

1	259	252	1
2	229	-158	15
3	116	-128	-1
4	88	177	-13
5	-143	1Ø5	-18

-12 8 L

1	-157	56	-17
2	119	-198	-14
3	1Ø5	26	5
4	259	224	8

-12 9 L

1	66	-27	2
2	178	-158	3
3	1Ø3	61	3
4	246	183	13

-12 1Ø L

1	-213	-52	-29
2	148	-168	-3

-12 11 L

1	2Ø7	-224	-3

-11 Ø L

1	-167	25	-19
2	286	299	-4
3	36	-132	-1Ø
4	322	-272	15
5	148	157	-1
6	2Ø3	139	12
7	-61	-135	-12
8	157	-132	3

-11 1 L

1	-43	175	-21
2	2Ø6	18Ø	6
3	337	-31Ø	9
4	15Ø	-69	1Ø
5	153	14Ø	2
6	96	9Ø	Ø
7	221	-135	16
8	-2Ø5	-79	-29

-11 2 L

1	319	269	17
2	-2Ø2	25	-29
3	257	-224	9
4	-97	-67	-9
5	238	186	12
6	-148	38	-14
7	179	-156	4
8	-187	63	-23

-11 3 L

1	45Ø	346	42
2	-148	-51	-17
3	212	-254	-12
4	-22	69	-3
5	231	191	9
6	37	-114	-7
7	-183	-69	-23
8	1ØØ	119	-2

-11 4 L

1	293	287	2
2	187	-186	Ø
3	-77	-153	-19
4	191	158	6
5	14Ø	12Ø	3
6	171	-161	2
7	-77	-18	-3
8	112	12Ø	-1

-11 5 L

1	162	196	-8
2	389	-3Ø3	32
3	-2ØØ	-78	-32
4	25Ø	236	3
5	-18Ø	17	-21
6	128	-175	-8
7	-185	4	-2Ø
8	112	119	Ø

-11 6 L

1	-2Ø5	95	-37
2	4ØØ	-335	25
3	-177	2	-21
4	246	244	Ø
5	-2Ø4	-49	-28
6	264	-217	12
7	-126	51	-1Ø
8	14Ø	181	-7

-11 7 L

1	-79	-54	-6
2	236	-238	Ø
3	133	144	-1
4	196	173	4
5	1Ø8	-173	-1Ø
6	8Ø	-181	-15
7	171	184	-2

-11 8 L

1	246	-232	3
2	194	-123	13
3	31Ø	296	4
4	-71	29	-3
5	271	-238	8
6	-155	-11	-14
7	227	2Ø4	4

-11 9 L

1	312	-272	12
2	62	-46	1
3	284	282	Ø
4	-1Ø6	-55	-8
5	2Ø2	-19Ø	2
6	-63	74	-5

-11 1Ø L

1	-145	9	-16
2	441	-367	33
3	-148	-44	-18
4	367	3Ø9	22
5	-185	-88	-3Ø
6	232	-197	9
7	44	141	-11
8	211	158	11
9	-66	-118	-1Ø
1Ø	-154	-1Ø1	-2Ø

-1Ø 4 L

1	-1Ø5	-138	-23
2	428	-371	25
3	123	173	-1Ø
4	312	264	16
5	-57	-183	-25
6	-98	-96	-12
7	2Ø7	192	3
8	55	95	-3
9	136	-144	-1
1Ø	-176	-38	-19

-1Ø 5 L

1	337	-322	6
2	22Ø	-255	-11
3	378	368	4
4	-116	132	-22
5	281	-213	19
6	-116	-38	-1Ø
7	317	247	21
8	-19Ø	2Ø	-23
9	291	-184	26
1Ø	-154	34	-14

-1Ø 6 L

1	423	-399	11
2	122	-1Ø8	2
3	479	427	24
4	-95	16	-6
5	333	-312	7
6	-99	54	-8
7	261	264	Ø
8	8Ø	-91	-1
9	9Ø	-153	-8
1Ø	97	74	2

-1Ø 7 L

1	282	-28Ø	Ø
2	1ØØ	111	-1
3	388	361	11
4	167	-185	-4
5	221	-249	-8
6	-75	154	-18
7	-13Ø	135	-21
8	-71	-139	-14
9	-148	-97	-18
1	328	-333	-1
2	19Ø	115	12
3	288	214	19
4	8Ø	-129	-5
5	184	-118	1Ø

-11 11 L

1	2Ø3	-21Ø	-1
2	193	251	-14
3	-187	96	-26
4	263	-212	11

-11 12 L

1	-87	-62	-6
2	276	3Ø2	-7

-1Ø Ø L

1	6Ø7	513	47
2	-111	-131	-21
3	447	-387	26
4	-161	141	-33
5	186	2Ø5	-4
6	-68	-58	-5
7	166	-2Ø3	-7
8	-64	71	-5
9	-12Ø	117	-16
1Ø	82	-126	-5

-1Ø 1 L

1	347	278	26
2	242	-261	-6
3	227	-238	-3
4	-141	98	-21
5	216	252	-1Ø
6	233	-181	12
7	2Ø4	-152	1Ø
8	127	13Ø	Ø
9	-57	51	-3
1Ø	151	-176	-4

-1Ø 2 L

1	19Ø	216	-7
2	448	-354	41
3	182	-223	-11
4	295	261	11
5	-171	65	-24
6	268	-2Ø9	16
7	-123	-1	-9
8	237	152	18
9	-212	-26	-29
1Ø	244	-183	13

-10 8 L

1	181	-179	0
2	307	278	10
3	177	171	1
4	369	-282	30
5	-62	-111	-10
6	170	187	-3
7	-185	25	-21
8	196	-183	2

-10 9 L

1	130	-170	-8
2	436	355	32
3	-195	52	-28
4	394	-340	20
5	-58	25	-2
6	278	199	19
7	-103	-60	-8
8	-77	-158	-17

-10 10 L

1	-103	38	-8
2	325	297	9
3	147	-93	7
4	300	-276	7
5	-99	132	-16
6	127	141	-2
7	72	-86	-1

-10 11 L

1	204	246	-11
2	139	181	-8
3	306	-274	9
4	164	-136	4
5	174	198	-4
6	-112	92	-11

-10 12 L

1	352	354	0
2	141	105	4
3	363	-349	4
4	-56	-83	-5

-10 13 L

1	369	332	12
2	70	-28	2
3	373	-316	17

-10 14 L

1	255	259	0

-9 0 L

1	89	-187	-21
2	462	-450	6
3	-81	18	-5
4	455	402	25
5	-117	-7	-10
6	323	-317	2
7	51	87	-3
8	216	226	-2
9	-45	-132	-12
10	145	-143	0
11	136	136	0
12	269	150	25

-9 1 L

1	145	-175	-7
2	511	-480	16
3	139	179	-9
4	482	459	12
5	218	-215	0
6	112	-204	-20
7	104	158	-9
8	65	168	-15
9	252	-230	6
10	-189	-60	-25
11	220	161	12
12	-114	95	-12

-9 2 L

1	335	-349	-6
2	220	-269	-18
3	302	319	-7
4	171	224	-15
5	309	-285	9
6	-174	-71	-27
7	256	264	-2
8	-178	-1	-22
9	294	-232	18
10	-180	10	-21
11	156	120	5
12	-209	37	-27

-9 3 L

1	482	-457	13
2	-193	-70	-37
3	515	451	33
4	-169	-50	-25
5	356	-322	14
6	-56	97	-9
7	236	241	-1
8	69	-85	-1
9	226	-190	8
10	-145	61	-15
11	172	128	7
12	-180	-74	-22

-9 4 L

1	490	-489	0
2	-159	105	-31
3	393	377	7
4	-110	-105	-18
5	283	-324	-16
6	211	188	6
7	248	229	5
8	238	-184	13
9	99	-143	-6
10	241	172	15
11	-228	69	-36
12	193	-131	10

-9 5 L

1	399	-399	0
2	319	341	-9
3	246	302	-21
4	325	-267	21
5	263	-294	-11
6	453	396	25
7	-43	115	-10
8	297	-256	12
9	-165	-54	-19
10	273	215	15
11	-180	10	-19

-9 6 L

1	242	-235	2
2	602	601	0
3	176	154	5
4	614	-555	31
5	-132	-15	-13
6	475	435	18
7	-159	-56	-20
8	192	-214	-5
9	-216	38	-32
10	186	180	1
11	14	-72	-2

-9 7 L

1	-51	225	-42
2	515	511	2
3	121	-128	-1
4	437	-443	-3
5	-78	159	-22
6	257	288	-10
7	186	-177	1
8	115	-149	-5
9	187	130	10
10	137	107	4

-9 8 L

1	448	424	11
2	286	287	0
3	326	-328	0

4	194	-232	-10
5	283	278	1
6	87	102	-1
7	227	-230	0
8	-47	-84	-5
9	-66	156	-16
10	94	55	3

-9 9 L

1	471	422	23
2	209	136	16
3	485	-458	12
4	-57	-55	-4
5	348	316	11
6	129	-26	9
7	261	-245	4
8	-155	2	-14
9	217	156	12

-9 10 L

1	361	370	-3
2	70	-48	1
3	441	-425	7
4	43	106	-6
5	277	260	4
6	103	-89	1
7	145	-203	-11
8	101	85	1

-9 11 L

1	157	223	-16
2	234	-286	-16
3	293	-275	5
4	157	206	-10
5	189	203	-3
6	254	-170	10
7	-44	-84	-5

-9 12 L

1	169	216	-10
2	378	-397	-7
3	82	-175	-14
4	275	306	-9
5	-62	92	-7
6	214	-223	-2

-9 13 L

1	-71	77	-6
2	382	-368	5
3	-89	-21	-4
4	334	312	6

-9 14 L

1	212	-173	8

2	284	-246	10

-8 0 L

1	487	-478	5
2	228	-285	-22
3	707	644	48
4	-171	-105	-35
5	467	-421	23
6	-138	46	-17
7	463	414	23
8	99	-91	1
9	373	-281	34
10	49	176	-18
11	263	217	12
12	121	-111	1
13	230	-168	13
14	41	89	-3

-8 1 L

1	580	-549	25
2	-195	28	-36
3	547	535	8
4	-89	-165	-29
5	432	-395	18
6	226	267	-14
7	352	393	-19
8	311	-333	-8
9	149	-165	-3
10	254	209	12
11	-109	149	-22
12	179	-131	8
13	142	-81	7
14	151	128	3

-8 2 L

1	405	-396	4
2	401	393	3
3	224	238	-4
4	289	-281	3
5	-54	-114	-13
6	484	474	5
7	178	135	9
8	336	-339	-1
9	-172	-98	-29
10	281	220	17
11	-194	26	-26
12	101	-158	-8
13	-109	65	-9
14	144	125	2

-8 3 L

1	-192	2	-35
2	585	558	21
3	-198	-50	-38
4	350	-283	29
5	-176	59	-30

6	565	489	46
7	-89	-115	-16
8	319	-318	0
9	-87	50	-7
10	247	166	20
11	-125	-106	-17
12	107	-106	0
13	100	111	-1

-8 4 L

1	-71	179	-33
2	445	422	12
3	-190	-54	-35
4	340	-319	9
5	134	178	-10
6	407	391	7
7	241	-293	-18
8	258	-252	1
9	116	159	-7
10	96	123	-3
11	106	-144	-5
12	-116	-78	-11
13	126	117	1

-8 5 L

1	253	271	-7
2	359	396	-18
3	321	-316	2
4	369	-373	-2
5	411	377	16
6	148	208	-15
7	382	-382	0
8	164	-197	-8
9	271	241	9
10	-154	95	-22
11	221	-164	12
12	101	-56	4
13	229	126	18

-8 6 L

1	580	571	5
2	-122	156	-34
3	639	-643	-3
4	164	-201	-10
5	441	430	5
6	-137	50	-16
7	455	-414	19
8	-103	13	-7
9	268	248	6
10	29	9	0
11	102	-165	-9
12	-63	19	-2

-8 7 L

1	505	522	-10
2	-182	-27	-30

3	717	-707	8					9	251	218	10		-7	5	L		10	-73	-105	-10	5	193	36	19
4	-55	91	-9		-8	12	L	10	329	322	2						11	283	250	9	6	347	288	17
5	407	407	0					11	66	-144	-11	1	504	518	-9		12	-150	85	-17	7	-135	-80	-13
6	181	-209	-7	1	383	-377	2	12	94	-150	-8	2	276	-298	-10									
7	353	-314	14	2	177	-179	0	13	23	146	-12	3	449	-444	3			-7	9	L			-7	14	L	
8	143	195	-11	3	275	305	-10	14	-53	52	-3	4	371	417	-24											
9	191	227	-9	4	-48	101	-7					5	352	343	4		1	586	-597	-8	1	145	29	12
10	103	-119	-2	5	304	-296	2		-7	2	L	6	397	-369	13		2	221	-220	0	2	311	327	-5
11	121	-163	-6	6	129	-28	8					7	270	-247	8		3	277	247	10	3	93	-8	5
12	140	172	-5	7	227	250	-5	1	348	396	-28	8	406	366	18		4	231	208	7	4	287	-276	2
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	-8	8	L		-8	13	L	3	159	-228	-23	10	234	-221	3		6	-157	-143	-34				
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1	224	283	-22	1	373	-392	-7	5	445	407	20	12	93	146	-7		8	68	77	0				
2	315	-323	-3	2	-31	-66	-3	6	268	260	3	13	-187	54	-23		9	276	-236	11	1	258	187	16
3	421	-412	4	3	334	310	7	7	479	-435	23	14	161	-165	0		10	-148	17	-13	2	134	210	-14
4	365	353	5	4	84	-29	3	8	288	-288	0						11	208	194	2	3	202	-190	2
5	219	251	-9	5	296	-280	4	9	434	386	22		-7	6	L									
6	317	-298	6	6	-140	52	-12	10	-142	63	-18							-7	10	L		-6	0	L
7	145	-186	-8					11	289	-238	16	1	498	506	-5									
8	273	290	-5		-8	14	L	12	-218	1	-33	2	555	-562	-4		1	685	-710	-19	1	711	734	-22
9	-103	126	-16					13	269	208	16	3	226	-283	-22		2	93	-77	2	2	264	331	-37
10	208	-204	0	1	303	-304	0	14	-87	-68	-7	4	397	406	-4		3	476	436	19	3	530	-520	9
11	-121	-50	-9	2	199	87	17	15	255	-200	12	5	-109	106	-19		4	-110	58	-11	4	192	-253	-24
				3	227	226	0					6	383	-388	-2		5	349	-308	15	5	-172	-63	-32
	-8	9	L	4	-26	-101	-6		-7	3	L	7	-119	-30	-12		6	-59	108	-10	6	451	-427	13
												8	337	275	23		7	289	249	12	7	-202	-98	-45
1	-57	147	-19		-8	15	L	1	619	581	34	9	-166	53	-22		8	39	-113	-6	8	-177	-18	-26
2	462	-499	-20					2	-95	93	-17	10	325	-308	6		9	256	-180	17	10	393	-378	6
3	-91	-56	-8	1	211	-192	3	3	452	-450	1	11	-96	7	-6		10	186	161	4	11	-191	38	-28
4	452	447	2	2	251	180	15	4	-163	-73	-30	12	208	238	-7						12	283	226	16
5	-74	65	-7					5	509	489	15	13	74	-85	-1			-7	11	L	13	-156	-80	-20
6	261	-299	-12		-7	0	L	6	-159	-25	-23										14	140	-152	-2
7	132	-42	9					7	472	-416	29		-7	7	L		15	522	-553	-17	15	80	94	-1
8	314	268	14	1	193	-256	-24	8	-58	20	-3						16	-37	95	-7				
9	-122	5	-9	2	618	588	26	9	419	377	19	1	307	338	-15			387	343	17		-6	1	L
10	205	-174	6	3	156	230	-24	10	134	-146	-2	2	591	-607	-13			62	-104	-4				
				4	348	-360	-5	11	196	-202	-1	3	-141	-42	-19			173	-169	0	1	922	913	7
	-8	10	L	5	130	-133	0	12	74	80	0	4	422	382	20			326	269	18	2	191	232	-17
				6	604	554	34	13	103	163	-9	5	-198	-71	-39			306	219	24	3	731	-706	23
1	-11	-47	-1	7	-46	-98	-9	14	-118	-132	-18	6	512	-477	18			248	-228	5	5	697	704	-6
2	338	-321	6	8	495	-488	3	15	124	-129	0	7	136	173	-8			113	-197	-14	6	246	-243	1
3	-146	49	-17	9	95	163	-13					8	357	328	11						7	547	-554	-4
4	468	443	11	10	379	335	18		-7	4	L	9	238	-210	7			-7	12	L	8	-114	72	-15
5	-106	-26	-8	11	-136	-50	-15					10	262	-238	7						9	382	412	-15
6	357	-325	11	12	223	-230	-1	1	436	455	-11	11	253	224	7		1	364	-388	-10	10	153	-194	-10
7	103	112	-1	13	-86	67	-7	2	-88	125	-22	12	199	136	11		2	305	346	-15	11	215	-186	7
8	203	201	0	14	200	156	8	3	760	-725	30	13	164	-123	6		3	198	223	-6	12	-91	154	-23
9	138	-150	-1	15	-85	-84	-8	4	229	263	-13						4	245	-239	1	13	-67	134	-15
								5	490	464	15		-7	8	L		5	-74	-88	-8	14	-29	-167	-18
	-8	11	L		-7	1	L	6	281	-286	-1						6	331	292	12	15	85	-110	-2
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1	260	-253	2	1	-140	-4	-19	8	322	281	16	2	497	-509	-7		8	298	-264	9				
2	277	-226	15	2	856	834	19	9	273	236	12	3	121	162	-9							-6	2	L
3	224	175	12	3	-159	6	-24	10	199	-245	-13	4	304	280	9			-7	13	L				
4	340	310	10	4	536	-496	33	11	116	-124	-1	5	206	-221	-4						1	500	520	-18
5	189	-203	-3	5	86	206	-29	12	140	94	6	6	367	-366	0		1	263	-219	12	2	88	-138	-12
6	182	-168	2	6	387	404	-8	13	94	95	0	7	323	290	12		2	453	470	-7	4	483	504	-14
7	286	237	13	7	301	-300	0	14	121	-140	-2	8	227	212	4		3	132	68	7	5	425	495	-45
8	106	94	1	8	436	-428	4					9	332	-288	14		4	418	-334	30	6	327	-351	-12

7	385	-416	-16
8	248	264	-6
9	34	143	-15
10	411	-365	21
11	-133	-47	-15
12	312	291	7
13	-124	31	-11
14	238	-240	0
15	-108	-32	-7
16	-77	201	-25

-6 3 L

1	383	396	-8
2	355	-409	-35
3	402	-442	-26
5	168	192	-7
7	-114	-190	-43
8	401	345	27
9	-150	-50	-21
10	420	-327	40
11	-219	66	-42
12	321	277	15
13	127	-74	6
14	268	-217	13
15	63	86	-1
16	92	142	-6

-6 4 L

1	-158	129	-45
2	1015	-980	29
3	-136	61	-23
5	-49	-90	-9
6	684	-654	25
7	132	198	-17
8	349	330	8
9	84	-191	-23
10	241	-213	8
11	123	163	-7
12	177	190	-2
13	90	-148	-8
14	104	-119	-1
15	118	140	-3

-6 5 L

1	329	-341	-6
2	1046	-1043	2
3	376	396	-11
5	419	-442	-12
7	314	338	-11
8	334	313	9
9	287	-213	25
10	175	-215	-10
11	406	341	26
12	-107	48	-9
13	253	-235	4
14	-135	6	-11
15	53	158	-12

-6 6 L

1	189	177	3
5	381	-379	1
6	221	-259	-14
7	466	468	-1
8	154	187	-8
9	441	-378	28
10	-49	71	-5
11	403	330	28
12	-132	-101	-18
13	298	-206	24
14	-85	37	-4

-6 7 L

2	-57	-63	-6
4	198	-173	7
5	368	-379	-5
6	61	87	-3
7	455	443	6
8	-61	-115	-13
9	302	-288	5
10	212	197	3
11	269	233	10
12	130	-168	-6
13	112	-182	-11
14	-49	108	-7

-6 8 L

1	540	-527	8
2	182	131	13
3	570	594	-17
4	148	-116	6
5	313	-344	-13
6	194	182	3
7	407	390	7
8	322	-288	12
9	139	-233	-23
10	316	278	12
11	139	148	-1
12	281	-250	8
13	44	-92	-3

-6 9 L

1	424	-461	-20
2	394	392	1
3	456	475	-10
5	161	-190	-7
6	215	224	-2
7	108	193	-17
8	307	-277	10
9	93	-81	1
10	214	224	-2
11	-142	0	-12
12	263	-222	9

-6 10 L

1	298	-320	-9
2	681	715	-27
3	235	223	3
4	367	-382	-6
5	111	50	7
6	242	219	7
7	-19	-143	-14
8	227	-217	2
9	109	112	0
10	182	186	0
11	237	-124	21

-6 11 L

1	142	-39	14
2	507	525	-9
3	94	-135	-7
4	384	-365	7
5	137	167	-6
6	360	322	14
7	191	-230	-9
8	298	-245	15
9	217	174	9
10	47	138	-9

-6 12 L

1	319	303	6
2	410	377	14
3	296	-303	-2
4	331	-300	11
5	207	224	-4
6	314	227	25
7	233	-220	3
8	204	-133	12
9	173	169	0

-6 13 L

1	478	499	-10
2	117	147	-5
3	407	-427	-8
4	194	-179	3
5	428	393	13
6	150	39	11
7	314	-310	1

-6 14 L

1	411	454	-18
2	319	46	52
3	474	-453	8
4	157	80	10
5	355	334	6
6	189	-150	6

-6 15 L

1	329	298	9
2	213	-213	0
3	286	-168	26
4	217	207	2

-6 16 L

1	205	179	5

-5 0 L

1	355	369	-9
2	193	-291	-53
3	300	-357	-36
4	665	679	-14
5	112	203	-29
7	198	-275	-31
9	-191	61	-36
10	541	-511	20
11	-99	-123	-20
12	457	390	31
13	-156	-95	-25
14	285	-233	15
15	-188	50	-25
16	175	198	-4
17	67	-83	-1

-5 1 L

1	418	473	-44
2	731	-776	-48
3	-149	158	-60
4	709	765	-58
5	79	-180	-27
7	-213	-29	-47
8	408	432	-13
9	-73	-189	-35
10	288	-341	-24
11	179	199	-5
12	281	279	0
13	227	-229	0
14	199	-176	5
15	-106	152	-21
16	132	161	-4
17	199	-150	8

-5 2 L

1	-145	68	-34
2	810	-876	-69
3	194	285	-48
4	581	614	-34
5	369	-443	-49
7	468	463	3
8	61	152	-17
10	-43	-136	-17
11	446	406	19
12	69	132	-9
13	395	-307	34
14	-65	-40	-3

15	203	231	-7
16	-235	28	-35
17	78	-143	-7

-5 3 L

1	763	-806	-45
2	297	-351	-35
3	339	388	-33
4	320	358	-23
5	500	-511	-9
6	178	-273	-39
8	-160	67	-27
9	378	-343	16
10	-95	4	-7
11	409	366	19
12	-187	-13	-27
13	359	-282	27
14	-82	67	-7
15	195	197	0
16	94	-47	3

-5 4 L

1	1148	-1217	-58
2	-83	-159	-39
3	763	787	-23
4	-120	-86	-24
7	326	259	29
8	-67	199	-38
9	409	-380	14
10	-44	89	-7
11	366	348	7
12	160	-164	0
13	240	-199	10
14	190	172	3
15	-104	108	-13
16	-140	-111	-18

-5 5 L

1	1275	-1311	-27
2	120	189	-23
3	907	938	-28
4	235	-236	0
6	230	256	-10
7	637	632	3
8	106	-169	-14
9	458	-433	13
10	458	434	11
11	-71	96	-10
12	349	-296	19
13	-101	-55	-8
14	299	222	21
15	-208	29	-27
16	81	-129	-5

-5 6 L

1	866	-881	-14
2	463	487	-20
3	674	682	-6
5	276	-326	-24
6	454	491	-22
7	303	345	-19
9	-54	-137	-17
10	494	434	29
11	-212	22	-35
12	381	-334	18
13	-87	16	-5
14	237	212	6
15	-212	-26	-27

-5 7 L

1	54	-112	-9
2	765	787	-20
3	171	141	8
5	-81	127	-20
6	506	529	-13
7	-127	-40	-15
8	461	-437	12
9	164	101	12
10	343	330	5
11	-79	-88	-9
12	327	-285	13
13	174	101	11
14	213	178	7

-5 8 L

1	22	17	0
3	128	-138	-2
4	648	-652	-3
5	340	334	3
6	477	447	15
7	256	-297	-15
8	372	-388	-7
9	263	271	-2
10	254	258	-1
11	261	-218	11
12	222	-209	3
13	214	198	3
14	-118	105	-14

-5 9 L

1	294	288	2
2	540	550	-5
3	255	-294	-15
4	397	-400	-5
5	311	336	-10
6	343	288	22
7	341	-280	23
8	200	-174	6
9	301	269	10
10	146	90	8
11	318	-279	12
12	86	-50	2
13	230	215	3

-5 10 L

1	593	627	-27
2	248	219	9
3	359	-320	17
4	34	20	0
5	369	348	9
6	72	-63	0
7	418	-372	19
8	85	98	-1
9	295	262	10
10	126	-133	-1
11	219	-168	10
12	-46	84	-5

-5 11 L

1	538	574	-21
2	143	-67	12
3	540	-553	-7
4	192	168	6
5	518	510	4
6	257	-206	14
7	328	-344	-5
8	217	165	11
9	115	147	-4
10	189	-145	8
11	-40	-97	-6

-5 12 L

1	406	404	1
3	437	-419	7
4	174	179	-1
5	373	373	0
6	277	-224	15
7	276	-262	4
8	236	177	13
9	262	117	28

-5 13 L

1	383	368	6
2	527	-511	7
3	254	-257	0
4	469	469	0
5	115	59	5
6	372	-343	10
7	-34	-70	-3
8	195	201	-1

-5 14 L

1	259	117	31
2	491	-515	-11
3	238	22	31
4	399	381	6
5	262	-85	32
6	359	-302	17

-5 15 L

1	216	-95	21
2	322	-264	17
3	247	191	12
4	266	244	5

-5 16 L

1	291	-285	1

-4 0 L

1	724	-760	-39
2	1071	-1147	-68
3	798	850	-55
4	195	280	-47
5	867	-931	-63
6	760	-795	-35
7	787	829	-40
8	340	376	-20
9	466	-505	-24
10	-69	-138	-20
11	583	554	22
12	-84	25	-6
13	413	-404	4
14	-203	-16	-32
15	376	319	21
16	-43	-54	-2
17	173	-191	-3
18	-75	61	-5

-4 1 L

1	1138	-1239	-86
2	161	-89	23
4	197	265	-36
5	954	-1007	-50
6	172	-206	-13
7	552	575	-19
8	-125	-63	-19
9	394	-397	-1
10	120	218	-27
11	529	520	5
12	236	-236	0
13	476	-440	17
14	257	215	12
15	90	231	-29
16	-89	-173	-23
17	123	-85	4
18	127	129	0

-4 2 L

1	1285	-1403	-90
2	263	370	-74
3	799	860	-64
4	178	-256	-39
5	733	-762	-30

6	637	653	-16
7	283	333	-26
8	436	-472	-22
9	328	-321	3
10	493	523	-18
11	228	218	3
12	445	-470	-13
13	195	-173	5
14	394	328	26
15	118	65	6
16	187	-182	1
17	89	-27	4

-4 3 L

1	871	-935	-67
2	476	465	12
3	1045	1118	-66
4	601	-637	-39
5	38	-143	-22
6	546	556	-10
7	-139	-17	-20
8	200	-226	-9
9	192	-223	-10
10	503	518	-8
11	-153	29	-20
12	487	-483	2
13	78	48	2
14	347	331	5
15	-168	-53	-20
16	222	-161	12
17	-179	43	-20

-4 4 L

1	-59	-127	-25
2	933	994	-60
3	-178	31	-44
4	551	-572	-21
5	-102	-80	-19
6	411	413	-1
7	-70	115	-17
8	362	-393	-16
9	-194	54	-37
10	395	409	-6
11	90	-176	-17
12	299	-280	6
13	146	180	-7
14	305	227	23
15	185	-138	8
16	48	-124	-7
17	142	93	6

-4 5 L

1	192	-262	-37
2	1262	1315	-39
3	105	-133	-7
4	885	-906	-18
5	180	239	-24

6	652	678	-25
7	253	-307	-24
8	155	-182	-7
9	268	265	1
10	254	238	5
11	340	-318	9
12	2	-155	-17
13	261	289	-9
14	-179	118	-31
15	277	-177	24
16	58	-56	0

-4 6 L

1	317	329	-7
2	795	825	-29
3	336	-365	-17
4	762	-775	-12
5	339	313	13
6	561	580	-12
7	510	-525	-11
8	107	-168	-13
9	429	420	4
10	160	196	-9
11	454	-392	28
12	75	-71	0
13	271	261	3
14	-19	22	0
15	217	-214	0
16	-162	45	-16

-4 7 L

1	787	819	-30
2	341	369	-16
3	798	-817	-18
4	235	-272	-15
5	646	649	-2
6	152	182	-8
7	504	-536	-18
8	-111	5	-10
9	419	424	-2
10	-147	-20	-17
11	398	-365	13
12	88	35	4
13	262	242	5
14	101	-83	1
15	256	-197	13

-4 8 L

1	947	954	-5
2	87	107	-3
3	794	-822	-24
4	156	134	5
5	804	817	-10
6	299	-334	-15
7	529	-549	-11
8	193	221	-8
9	435	364	31

10	265	-247	6
11	241	-271	-9
12	193	145	9
13	252	171	18
14	170	-153	2

-4 9 L

1	676	660	13
2	294	-298	-1
3	579	-586	-4
4	141	209	-19
5	497	498	0
6	341	-296	18
7	349	-354	-2
8	373	362	5
9	230	183	12
10	424	-368	22
11	42	-80	-2
12	174	185	-2
13	119	49	6

-4 10 L

1	147	128	4
2	384	-324	27
3	138	-45	13
4	512	543	-17
5	162	-37	18
6	446	-456	-5
7	141	1	14
8	303	293	3
9	-159	-34	-18
10	286	-238	14
11	68	33	2
12	288	203	20

-4 11 L

1	-56	-82	-8
2	541	-555	-7
3	-50	3	-2
4	641	610	20
5	168	-124	9
6	465	-444	9
7	-65	100	-9
8	350	289	20
9	203	-156	9
10	157	-172	-2
11	225	169	11

-4 12 L

1	242	37	39
2	633	-636	-1
3	221	170	13
4	536	531	2
5	258	-274	-5
6	340	-318	7
7	237	221	4

8	301	205	25
9	227	-209	4
10	140	-102	4

-4 13 L

1	435	-405	13
2	340	-255	29
3	499	470	13
4	220	149	15
5	399	-380	7
6	222	-135	17
7	295	256	11
8	34	40	0

-4 14 L

1	426	-429	-1
2	254	-74	33
3	448	394	21
4	207	-35	23
5	406	-350	20
6	-45	68	-3
7	285	294	-2

-4 15 L

1	289	-248	11
2	255	94	30
3	372	357	5
4	170	-121	7

-4 16 L

1	289	-288	19
2	237	203	7

-3 0 L

9	294	-391	-55
10	410	425	-9
11	91	205	-28
12	476	-436	21
13	-147	0	-17
14	497	509	-5
15	-211	-37	-35
16	207	-225	-4
17	-119	64	-11
18	251	152	20

-3 1 L

9	-163	55	-30
10	607	605	2
11	-159	61	-25
12	473	-481	-4
13	216	275	-20
14	324	343	-8
15	231	-179	13
16	239	-197	10

17	179	163	2		-3	5	L		2	594	-594	0	11	215	224	-2		-2	1	L					-2	5	L		
18	-124	123	-18						3	164	46	22																	
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	-3	2	L	2	178	-266	-46		5	154	-80	14						11	584	-586	-2	1	123	-18	20					
				3	972	-993	-18		6	749	-759	-8	1	766	-756	6		12	-192	-56	-36	2	1258	-1244	10					
1	-302	-61	-139	4	60	162	-26		7	-87	4	-6	2	178	27	22		13	397	397	0	3	242	-269	-15					
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7	326	-349	-13	6	87	-161	-18		9	197	-203	-1	4	211	-109	21		15	219	-271	-16	5	246	-212	15					
8	410	-413	-2	7	460	-503	-27		10	415	-368	20	5	497	-459	17		16	206	211	-1	6	581	-541	36					
9	389	413	-14	8	479	502	-14		11	211	174	9	6	296	278	5		17	226	200	6	7	325	342	-9					
11	-142	-167	-42	9	191	198	-2		12	207	221	-3	7	377	342	12		18	212	-166	9	8	657	661	-3					
12	370	-383	-6	10	373	-395	-11		13	151	-108	6	8	225	-238	-3		19	168	-130	6	9	327	-365	-19					
13	424	426	-1	11	254	-274	-7		14	94	-126	-3	9	216	-192	5						10	519	-518	0					
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	-3	3	L						3	217	-51	36	3	335	292	15		12	-115	127	-25	17	276	-234	10					
					-3	6	L		4	680	682	-1	4	277	-283	-2		13	268	284	-6									
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3	543	-542	0	2	255	-258	-1		7	425	429	-2	7	232	118	21		16	302	267	11	1	263	-214	25					
4	240	-301	-37	3	752	-765	-12		8	309	282	9	8	263	-258	1		17	154	151	0	2	992	-988	2					
5	248	258	-5	4	380	385	-3		9	261	-265	-1						18	291	-244	12	4	1032	997	29					
6	938	947	-8	5	682	691	-8		10	221	-182	9		-3	14	L						5	692	-665	25					
7	539	-548	-7	6	552	-555	-3		11	237	219	4							-2	3	L	6	794	-800	-5					
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15	330	-321	3	14	272	-213	16		2	186	-53	25						14	311	-263	16	14	-130	-3	-11					
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	-3	4	L						7	397	377	9	3	186	-3	18													
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1	816	841	-27	2	434	-448	-9		9	270	-273	-1										2	592	-573	18					
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3	864	-901	-38	4	554	555	0		11	307	261	13						1	446	507	-73	4	218	237	-7					
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14	97	-188	-17	15	84	134	-6		6	165	95	12	16	-206	31	-31		13	-146	18	-17	15	278	243	9					
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1	85Ø	-826	21	1Ø	317	312	1	17	-1Ø1	-23	-7	4	199	286	-5Ø	6	8Ø6	8Ø2	3	13	3Ø6	261	12
2	291	-237	24	11	193	-42	19	18	258	-213	11	5	56Ø	-573	-13	7	372	386	-7				
3	965	93Ø	29	12	259	-167	19	19	34	-9	Ø	6	482	-5Ø2	-18	8	572	-6Ø3	-19		-1	11	L
4	238	168	23									7	559	5Ø5	44	9	218	-166	15				
5	763	-741	19		-2	12	L		-1	1	L	8	2Ø4	237	-13	1Ø	547	525	12	1	661	67Ø	-6
6	99	68	4									9	778	-747	27	11	44	1Ø5	-6	2	336	352	-7
7	623	597	19	1	215	-66	29	9	26Ø	312	-28	1Ø	42	-1Ø6	-8	12	462	-424	17	3	463	-464	Ø
8	236	-233	1	2	599	595	2	1Ø	11Ø2	-11ØØ	1	11	494	517	-13	13	-18Ø	5	-22	4	137	-82	8
9	393	-397	-1	3	239	-89	32	11	-19	154	-22	12	-117	85	-17	14	345	357	-4	5	318	3Ø6	4
1Ø	-151	-9	-17	4	499	-499	Ø	12	488	533	-27	13	428	-4Ø7	1Ø	15	-98	8	-5	6	151	-32	15
11	314	353	-15	5	2Ø6	164	1Ø	13	-125	-146	-31	14	-142	45	-16	16	274	-221	13	7	378	-3ØØ	28
12	-76	-86	-8	6	373	35Ø	8	14	431	-4Ø9	1Ø	15	189	221	-8					8	15	-75	-3
13	261	-234	7	7	132	-14Ø	-1	15	-165	116	-32	16	-139	-133	-24		-1	8	L	9	357	35Ø	2
14	81	129	-5	8	287	-269	5	16	279	294	-5	17	262	-142	25					1Ø	191	26	2Ø
15	161	178	-3	9	233	187	1Ø	17	129	-156	-4	18	225	151	14	1	564	-532	25	11	35Ø	-27Ø	23
				1Ø	263	237	6	18	3Ø1	-246	15					2	1Ø81	1Ø34	37				
	-2	9	L					19	257	181	16		-1	5	L	3	292	281	5		-1	12	L
					-2	13	L									4	566	-535	23				
1	8Ø8	-756	44						-1	2	L	1	813	-769	45	5	-35	5	-1	1	618	625	-4
2	193	63	28	1	37Ø	3Ø4	25					2	895	-86Ø	33	6	638	62Ø	12	2	165	-5Ø	17
3	591	551	25	2	456	447	3	1	2Ø5	-64	51	3	263	324	-39	7	163	81	15	3	63Ø	-588	22
4	229	-231	Ø	3	255	-125	29	2	168	183	-6	4	34Ø	-35Ø	-6	8	568	-577	-6	4	75	12	3
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9	22Ø	-254	-1Ø	8	246	-192	12	12	357	342	7	11	444	414	15	13	121	69	6	9	319	245	21
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11	2Ø1	147	11					14	357	-358	Ø	13	356	-315	16	15	-48	-97	-6				
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13	65	-71	Ø					16	21Ø	186	5	15	244	224	5		-1	9	L				
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				4	174	-129	7						-1	6	L	4	789	-751	3Ø	4	296	2Ø2	26
1	4Ø8	-418	-5	5	277	284	-2		-1	3	L					5	25Ø	257	-2	5	296	246	14
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3	387	4Ø2	-7	7	282	-261	5	1	148	-159	-4	2	145	95	14	7	117	-176	-13	8	252	222	7
4	36Ø	-312	21					2	834	-832	2	3	1Ø91	1Ø76	12	8	292	-284	3				
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6	453	4Ø5	22					5	366	-42Ø	-42	5	8Ø2	-777	23	1Ø	269	257	3				
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8	369	-352	6	2	3Ø5	1ØØ	42	7	68Ø	683	-2	7	731	698	29	12	271	-214	15	2	376	-382	-2
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	-2	11	L					14	166	-217	-13	14	316	3Ø8	2	2	298	321	-1Ø				
					-1	Ø	L	15	238	234	1	15	216	121	18	3	237	-195	13	1	326	124	45
1	3Ø3	-228	27					16	-2Ø	95	-6	16	179	-191	-2	4	427	-386	2Ø	2	465	-413	2Ø
2	67Ø	657	9	9	634	629	5	17	119	-191	-13	17	87	-62	1	5	354	355	Ø	3	218	-32	24
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6	377	383	-2	13	-135	137	-32					1	913	-887	23	9	393	417	-1Ø				
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8	344	-316	1Ø	15	-145	-14Ø	-32	2	748	-787	-44	3	829	785	39	11	4Ø2	-368	12	1Ø	632	-62Ø	11
9	178	1ØØ	12	16	377	331	18	3	621	626	-5	5	833	-794	33	12	-82	-28	-4	11	52Ø	549	-27

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13	482	-495	-10	5	670	-676	-9	-16	304	304	0	3	258	-244	11	-17	421	362	32	4	345	-319	17
14	132	-187	-19	6	436	-458	-31	-15	330	-320	5	4	563	-540	30	-16	73	-149	-16	5	735	727	8
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19	380	398	-6
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3	857	820	35
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5	560	-513	45
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8	566	537	22
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17	565	-560	2
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19	354	367	-4
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	9 5 L			7	7Ø	-184	-15													15	43Ø	431	Ø
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7	-116	-1Ø1	-14	6	174	-1Ø8	9		1Ø -11 L							15	-124	-13Ø	-2Ø	12	74	221	-28
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9	-9Ø	-12	-4	8	-89	86	-8	Ø	393	-334	22					17	-78	-94	-8	14	-55	-184	-23
1Ø	264	3Ø5	-11	9	411	-438	-1Ø	1	247	-216	8	Ø	256	-237	6					15	397	416	-7
11	119	-149	-4	1Ø	193	-95	14	2	423	479	-26	1	175	218	-11		1Ø -5 L			16	-7Ø	111	-1Ø
								3	257	232	7	2	367	362	2					17	3Ø3	-333	-9
	9 6 L				1Ø -14 L			4	631	-645	-7	3	382	-375	3	Ø	279	332	-21				
								5	138	-2Ø6	-15	4	233	-213	6	1	5Ø2	481	11		1Ø -2 L		
-8	216	-189	5	Ø	193	179	2	6	698	721	-14	5	551	594	-24	2	536	-528	4				
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-5	-128	132	-2Ø	3	331	388	-2Ø	9	137	141	Ø	8	-64	45	-4	5	335	353	-8	2	223	-247	-8
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	1Ø	-1	L	9	-75	-53	-5	-7	-139	-38	-12	9	74	95	-1	2	131	52	9	3	-147	-9	-16
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16	-156	-98	-19		11	-1	L		-7	-113	55	-8	3	-169	-143	-28					5	24Ø	-263	-6
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	11	-4	L						-5	138	-15Ø	-1		12	-13	L	1	-11Ø	-31	-8	7	375	354	8
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14	393	42Ø	-1Ø		11	Ø	L		11	256	-261	-1	5	242	236	1					5	-123	-11Ø	-18
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3	343	294	18	2	2Ø7	237	-7		1	149	188	-7	2	339	-319	6	9	641	-623	8				
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11	-135	151	-26	1Ø	3	122	-8			11	5	L	1Ø	467	-457	4					5	-254	47	-48
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13	1Ø5	169	-1Ø	12	-59	-57	-3		-1	11Ø	-94	1	12	356	4Ø2	-16	1	424	-376	18	7	14Ø	-198	-12
14	-95	175	-23						Ø	85	129	-5	13	378	-4Ø1	-8	2	-38	-3	Ø	8	314	-27Ø	13
15	71	-97	-2		11	2	L		1	2Ø6	148	1Ø					3	399	35Ø	18	9	215	199	3
									2	255	-23Ø	6		12	-9	L	4	88	-112	-3	1Ø	4Ø9	412	-1

11	360	-302	18
12	219	-270	-13
13	371	336	11

12 -2 L

0	300	-233	19
1	138	148	-1
2	244	213	8
3	141	-129	2
4	-28	-189	-23
5	184	235	-12
6	169	197	-6
7	309	-321	-3
8	30	-127	-9
9	250	270	-5
10	-155	122	-23
11	321	-299	6
12	-234	46	-35

12 -1 L

0	241	-168	16
1	315	212	29
2	-98	94	-11
3	235	-209	6
4	-120	-93	-14
5	367	320	16
6	64	84	-1
7	327	-302	8
8	-35	-82	-4
9	352	310	13
10	-176	-89	-23
11	230	-192	8
12	92	79	1

12 0 L

0	-78	-66	-6
1	323	235	25
2	-203	-2	-26

3	289	-254	10
4	-73	-15	-3
5	402	366	13
6	-130	-70	-13
7	284	-307	-7
8	-139	88	-16
9	313	243	19
10	184	-135	8

12 1 L

-4	-91	-10	-4
-3	173	203	-6
-2	-92	-8	-4
-1	276	-219	14
0	69	65	0
1	235	210	6
2	126	-117	1
3	318	-293	7
4	283	239	11
5	270	246	6
6	300	-260	11
7	185	-237	-11
8	253	253	0
9	32	144	-10

12 2 L

-2	-164	-65	-18
-1	95	-129	-4
0	-104	104	-12
1	193	176	3
2	284	-256	7
3	155	-169	-2
4	351	327	7
5	-173	42	-18
6	131	-256	-26
7	47	-76	-1

12 3 L

1	-148	42	-13
2	352	-260	26
3	-163	-8	-15

13 -11 L

3	281	267	3
4	215	239	-5
5	322	-321	0
6	213	-190	4
7	271	297	-7
8	-146	120	-20

13 -10 L

0	296	-272	6
1	-153	-111	-20
2	303	329	-7
3	18	76	-3
4	454	-391	23
5	-145	4	-12
6	352	322	9
7	-113	-96	-12
8	413	-384	10
9	199	192	1

13 -9 L

0	-153	30	-14
1	293	-256	10
2	-74	20	-3
3	329	282	14
4	-103	-51	-7
5	302	-306	-1
6	-93	76	-8
7	171	204	-6
8	-145	-82	-16
9	298	-297	0
10	113	218	-19
11	201	219	-3

13 -8 L

0	-63	-112	-9
1	174	-250	-17
2	146	150	0
3	267	243	6
4	149	-211	-12
5	135	-180	-8
6	198	182	3
7	132	149	-2
8	219	-223	0
9	-62	-158	-16
10	211	287	-20
11	77	113	-3

13 -7 L

0	245	-225	4
1	207	-207	0
2	287	230	15
3	-58	142	-14
4	377	-302	24
5	-98	-72	-8
6	424	300	16
7	-134	50	-12
8	448	-378	26
9	-172	38	-18
10	327	337	-3
11	-200	-73	-27
12	318	-301	5

13 -6 L

0	209	-236	-6
1	97	-132	-4
2	352	286	20
3	124	-31	8
4	355	-317	12
5	-149	103	-20
6	447	396	19
7	-121	-116	-17

8	298	-295	0
9	82	107	-2
10	343	332	3
11	134	-191	-10
12	166	-208	-8

13 -5 L

0	337	-283	16
1	107	78	3
2	284	257	7
3	254	-210	11
4	205	-192	3
5	217	241	-6
6	325	301	7
7	329	-302	8
8	191	-185	1
9	219	229	-2
10	144	228	-17
11	271	-287	-4

13 -4 L

0	275	-209	16
1	218	220	0
2	-95	141	-17
3	317	-237	22
4	60	-126	-7
5	449	383	24
6	78	70	0
7	414	-375	14
8	-239	-56	-38
9	365	376	-3
10	-112	3	-7
11	452	-434	6

13 -3 L

0	130	-58	7
1	277	237	10
2	-105	54	-8

3	155	-208	-10
4	-179	16	-20
5	352	329	7
6	-74	-128	-12
7	283	-331	-15
8	-126	67	-11
9	420	386	12
10	258	-245	3

13 -2 L

0	139	48	9
1	200	189	2
2	-172	-42	-18
3	219	-172	9
4	198	192	1
5	27	164	-15
6	221	-206	3
7	225	-234	-2
8	194	188	1
9	-76	130	-12

13 -1 L

0	42	130	-8
1	153	115	5
2	70	-98	-2
3	173	-158	2
4	297	244	14
5	-165	93	-21
6	331	-247	23
7	-169	-116	-24
8	295	241	13

13 0 L

1	-86	86	-8
2	237	-210	6
3	-187	-73	-23
4	271	273	0
5	-222	-39	-30

Appendix C. Structure factor amplitudes ($10F_o$, $10F_c$, $10\sigma_F$; $\sigma_F/k = [F_o + \sigma_{F^2}]^{\frac{1}{2}} - |F_o|$, $k = 1.0108$; $F_o < 0$ means $I_o < 0$) for *trans*-Os(η^2-HBA-TMI)$_2$Cl$_2$.

-13 Ø L

2	163	135	8
4	198	187	4
6	224	198	11
8	226	223	1
10	174	201	-10
12	193	186	2

-13 1 L

1	183	184	Ø
2	-83	1	-7
3	213	180	13
4	71	53	2
5	166	162	1
6	-106	-5	-12
7	218	204	5
8	30	22	Ø
9	200	220	-8
10	68	72	Ø
11	159	169	-3
12	52	33	1

-13 2 L

2	168	168	Ø
3	102	37	9
4	194	163	11
5	-66	6	-4
6	184	173	4
7	80	13	6
8	195	200	-2
9	-95	39	-11
10	177	191	-5
11	-86	33	-8

-13 3 L

3	127	165	-10
4	-85	50	-10
5	134	141	-1
6	52	14	2
7	191	160	11
8	-15	6	Ø
9	193	191	Ø
10	61	34	2

-13 4 L

6	163	188	-8
7	83	1	7

-12 Ø L

2	189	194	-2
4	221	189	14
6	295	309	-8
8	319	328	-5
10	230	260	-14
12	260	278	-9
14	206	222	-6

-12 1 L

1	272	253	10
2	-69	61	-9
3	223	197	11
4	-63	32	-6
5	188	188	Ø
6	-43	-63	-7
7	239	279	-20
8	-35	-60	-5
9	289	319	-18
10	106	12	13
11	220	259	-18
12	-33	-10	-1
13	222	222	Ø
14	101	-46	8
15	265	256	4

-12 2 L

1	33	97	-9
2	214	242	-12
3	134	34	19
4	215	212	1
5	-14	25	-1
6	195	237	-19
7	25	-33	Ø
8	245	263	-9
9	-122	48	-19
10	216	263	-23
11	Ø	72	-5
12	198	215	-7
13	61	2	4
14	176	219	-16
15	-83	12	-6

-12 3 L

1	231	213	7
2	60	79	-2
3	235	259	-11
4	51	64	-1
5	264	266	-1
6	-49	-10	-2
7	201	219	-8
8	51	29	2
9	205	222	-7
10	126	76	10
11	177	204	-10
12	97	17	9
13	247	217	13
14	59	12	3

-12 4 L

1	-15	15	Ø
2	196	186	3
3	34	31	Ø
4	268	264	2
5	39	-19	1
6	180	198	-7
7	-87	16	-8
8	189	169	7
9	78	41	4
10	183	213	-11
11	-37	32	-2
12	202	240	-15
13	38	32	Ø

-12 5 L

1	153	120	9
2	58	4	3
3	224	188	14
4	-107	29	-12
5	229	228	Ø
6	-87	13	-8
7	199	221	-9
8	-168	26	-30
9	216	211	1
10	118	47	12
11	250	278	-13
12	119	69	9

-12 6 L

2	61	164	-21
3	38	50	-1
4	230	228	Ø
5	84	44	5
6	199	231	-13
7	-155	37	-26
8	207	193	5
9	22	1	Ø
10	218	208	3

-11 Ø L

2	246	240	3
4	355	372	-13
6	483	484	Ø
8	364	399	-26
10	216	227	-5
12	245	275	-16
14	321	316	2
16	217	272	-25

-11 1 L

1	374	380	-4
2	93	104	-3
3	324	333	-6
4	127	54	17
5	297	312	-9
6	-76	-6	-7
7	371	395	-18
8	-33	-43	-3
9	373	387	-10
10	59	-10	4
11	233	266	-17
12	-117	-49	-19
13	335	334	1
14	80	-105	-4
15	334	346	-7
16	79	27	5
17	276	272	2

-11 2 L

1	-113	-16	-16
2	327	343	-10
3	101	47	10
4	298	306	-5
5	-86	18	-9
6	303	327	-16
7	31	67	-4
8	322	350	-19
9	97	101	-1
10	332	348	-10
11	-114	-7	-15
12	314	325	-7
13	122	-56	13
14	299	336	-21
15	-69	-37	-6
16	275	301	-13
17	41	70	-3

-11 3 L

1	282	234	26
2	73	80	-1
3	349	354	-3
4	90	-7	10
5	269	312	-26
6	-42	-22	-2
7	265	295	-18
8	63	75	-2
9	342	346	-3
10	-109	86	-22
11	349	365	-10
12	36	-9	1
13	248	233	7
14	37	-19	1
15	266	267	Ø
16	-41	105	-12
17	232	258	-11

-11 4 L

1	81	66	2
2	277	284	-4
3	-59	29	-5
4	233	279	-24
5	107	-55	11
6	253	290	-21
7	Ø	-10	Ø
8	242	282	-21
9	78	38	5
10	320	310	6
11	-25	34	-2
12	299	328	-17
13	21	10	Ø
14	250	267	-8
15	139	54	17
16	153	211	-20

-11 5 L

1	237	210	12
2	-66	39	-6
3	271	291	-10
4	54	51	Ø
5	328	316	8
6	-98	21	-11
7	162	220	-24
8	56	46	1
9	247	262	-7
10	80	50	4
11	330	312	11
12	-85	39	-9
13	213	257	-19
14	38	51	-1
15	157	184	-8

-11 6 L

1	43	57	-1
2	230	239	-4
3	-45	70	-7
4	296	302	-3
5	-63	112	-18
6	281	275	3
7	-86	64	-12
8	268	250	9
9	-64	7	-4
10	294	286	4
11	116	36	13
12	266	304	-19
13	-56	38	-4

-11 7 L

1	270	244	12
2	-88	4	-8
3	226	252	-11
4	-91	60	-12
5	261	255	2
6	97	92	1
7	272	288	-8
8	153	40	23
9	312	294	9
10	90	5	8
11	268	269	Ø
12	88	16	7

-11 8 L

3	-111	15	-12
4	186	240	-21
5	123	86	7
6	299	275	12
7	93	60	5
8	228	214	5

-10 Ø L

12	377	382	-4
14	429	411	14
16	281	277	1
18	243	226	7

-10 1 L

12	-86	-34	-11
13	397	378	14
14	45	21	1
15	346	383	-24
16	21	24	Ø
17	233	241	-3
18	98	24	9
19	240	228	5

-10 2 L

11	70	-9	6
12	394	411	-12
13	-73	-24	-7
14	370	391	-14
15	25	-14	Ø
16	355	339	9
17	-34	54	-4
18	312	301	5

-10 3 L

10	117	112	1
11	394	399	-4
12	-100	-51	-15
13	372	357	11
14	61	-8	4
15	360	363	-2
16	132	80	11
17	384	379	3
18	-118	17	-13

-10 4 L

1	84	79	1
2	351	360	-6
8	400	391	7
9	172	115	20
10	432	436	-3
11	-24	-13	Ø
12	361	375	-9
13	111	-39	12
14	295	297	-1

15	-72	59	-9
16	265	291	-13
17	-105	5	-11

-10 5 L

1	310	315	-2
2	-94	34	-12
3	423	435	-9
4	-77	70	-13
5	375	356	14
6	77	62	2
7	305	315	-6
8	136	60	19
9	399	400	0
10	-31	0	-1
11	376	389	-9
12	95	60	6
13	264	288	-13
14	-88	9	-8
15	209	208	0
16	54	3	2
17	278	251	12

-10 6 L

1	-61	30	-5
2	373	388	-11
3	31	77	-6
4	344	351	-5
5	-14	57	-4
6	315	307	5
7	-55	0	-3
8	334	305	19
9	-85	61	-12
10	384	389	-3
11	51	110	-10
12	361	369	-5
13	85	95	-1
14	220	236	-6
15	-70	50	-7
16	208	210	0

-10 7 L

1	284	300	-9
2	0	29	0
3	292	300	-4
4	-58	105	-16
5	296	297	0
6	128	140	-3
7	285	301	-8
8	33	22	0
9	326	339	-7
10	-118	49	-17
11	323	336	-7
12	0	67	-4
13	276	275	0
14	-22	20	0

-10 8 L

1	72	17	5
2	212	228	-6
3	-26	56	-4
4	296	324	-15
5	108	117	-2
6	297	298	0
7	-71	32	-6
8	258	240	9
9	116	-60	10
10	224	199	10
11	68	-1	4
12	196	238	-16

-10 9 L

1	210	216	-2
2	-70	45	-6
3	209	209	0
4	128	95	7
5	233	233	0
6	110	19	12
7	171	224	-19
8	67	-18	4
9	183	221	-14

-9 0 L

14	550	557	-5
16	383	382	0
18	296	269	14
20	299	295	1

-9 1 L

14	78	32	6
15	406	412	-4
16	-57	73	-9
17	222	263	-20
18	-110	19	-13
19	230	250	-8
20	-72	-21	-5

-9 2 L

14	421	427	-4
15	0	67	-5
16	306	311	-2
17	62	70	-1
18	285	276	4
19	-51	28	-3
20	325	265	30

-9 3 L

13	344	342	1
14	121	-12	17
15	375	399	-16
16	146	78	17
17	397	396	0
18	-65	-10	-4
19	316	290	13

-9 4 L

12	367	363	3
13	-75	44	-9
14	327	335	-4
15	-111	88	-22
16	340	348	-4
17	-67	-19	-5
18	318	316	0
19	-107	-78	-16

-9 5 L

11	439	436	2
12	-56	16	-4
13	326	332	-4
14	96	55	7
15	276	290	-7
16	-142	33	-22
17	342	347	-2
18	166	3	27

-9 6 L

1	62	59	0
8	404	407	-2
9	30	0	1
10	422	437	-11
11	20	39	-1
12	384	381	2
13	46	71	-3
14	280	287	-3
15	21	1	0
16	251	274	-11
17	92	32	7

-9 7 L

1	262	285	-13
2	-87	-36	-10
3	330	351	-14
4	73	101	-6
5	343	331	8
6	122	93	7
7	392	374	13
8	61	3	4
9	399	405	-4
10	-62	58	-8
11	271	297	-14
12	-77	79	-13
13	250	249	0
14	110	-23	12
15	203	229	-10
16	-101	-15	-10

-9 8 L

1	92	-16	9
2	283	286	-1
3	113	74	8
4	350	345	3
5	127	127	0
6	351	363	-8
7	60	54	0
8	226	246	-9
9	116	-40	13
10	226	223	1
11	126	71	11
12	278	281	-1
13	131	55	15
14	243	251	-3

-9 9 L

1	242	220	10
2	-86	58	-12
3	243	243	0
4	100	59	7
5	315	291	13
6	-67	-16	-5
7	301	283	10
8	-40	-24	-2
9	243	265	-10
10	-53	54	-6
11	254	286	-16
12	67	92	-3

-9 10 L

1	-61	9	-4
2	172	147	8
3	86	-22	7
4	190	177	5
5	107	57	8
6	264	271	-3
7	109	68	7
8	223	238	-6
9	112	70	7

-8 0 L

16	264	278	-7
18	326	335	-5
20	411	374	24

-8 1 L

16	-108	13	-14
17	294	278	9
18	62	-16	4
19	316	325	-5
20	-15	-46	-2
21	315	328	-6

-8 2 L

15	-82	60	-12
16	346	336	7
17	-88	-6	-8
18	272	281	-4
19	-88	2	-8
20	274	274	0

-8 3 L

15	447	454	-5
16	42	57	-1
17	429	449	-14
18	-71	-51	-8
19	261	254	3
20	-104	-20	-11

-8 4 L

14	352	359	-5
15	125	114	3
16	449	442	5
17	39	21	1
18	376	366	6
19	87	-56	4

-8 5 L

13	281	268	8
14	-91	38	-11
15	332	346	-8
16	-142	61	-26
17	372	357	10
18	21	-4	0
19	219	255	-15

-8 6 L

11	137	85	14
12	307	326	-12
13	67	-52	2
14	344	327	11
15	107	-61	8
16	262	285	-12
17	-134	-34	-19
18	248	259	-5

-8 7 L

9	416	421	-4
10	98	47	9
11	368	343	17
12	35	45	0
13	298	294	2
14	137	-35	19
15	282	293	-6
16	37	-53	-1
17	245	265	-9

-8 8 L

1	-67	56	-9
2	359	364	-3
3	70	122	-12
4	454	454	0
5	125	85	10
6	353	370	-12
7	-114	-47	-17
8	287	291	-2
9	72	-12	6
10	295	312	-10
11	32	104	-11
12	301	335	-20
13	143	96	11
14	260	303	-22
15	-71	-2	-5
16	213	266	-22

-8 9 L

1	274	253	11
2	96	28	10
3	264	281	-9
4	73	49	3
5	349	354	-3
6	-43	-22	-2
7	268	276	-4
8	-55	-38	-5
9	268	249	10
10	-125	70	-21
11	307	301	3
12	-70	71	-10
13	326	310	9
14	-154	24	-22

-8 10 L

1	-168	-12	-29
2	213	172	17
3	42	67	-2
4	260	276	-8
5	-76	56	-10
6	330	317	7
7	-79	9	-7
8	188	251	-26
9	-78	12	-6
10	178	217	-15
11	-44	2	-1
12	260	312	-24

-8 11 L

1	241	204	16
2	117	45	12
3	314	284	16
4	133	56	15
5	315	307	4
6	-41	86	-8
7	231	259	-12
8	97	106	-1

-7	0	L	
2	564	508	43
4	876	967	-71
6	557	579	-17
18	319	315	2
20	359	369	-6

-7	1	L	
1	451	436	16
2	182	-176	4
3	608	661	-63
4	45	-56	-2
5	803	901	-111
6	44	15	3
7	677	745	-78
17	311	312	-1
18	-126	-33	-18
19	377	355	14
20	-111	20	-13
21	367	338	16

-7	2	L	
1	70	88	-6
2	552	572	-23
3	118	-125	-3
4	709	745	-41
5	58	-66	-1
6	764	846	-93
17	121	-35	16
18	326	355	-18
19	-90	14	-9
20	316	313	1
21	107	9	11

-7	3	L	
16	-67	12	-5
17	432	426	4
18	-109	-56	-16
19	289	308	-9
20	46	26	1
21	240	186	20

-7	4	L	
15	-80	69	-13
16	458	471	-9
17	99	-23	10
18	355	367	-7
19	120	-75	9
20	254	248	2

-7	5	L	
14	128	55	17
15	422	425	-1
16	-109	13	-13
17	366	373	-4
18	52	-9	2
19	196	205	-3

-7	6	L	
13	-90	-66	-15
14	332	367	-23
15	111	-35	13
16	339	351	-7
17	-82	2	-7
18	212	228	-6
19	63	10	3

-7	7	L	
11	303	323	-13
12	-46	69	-8
13	304	307	-1
14	122	-97	6
15	345	374	-19
16	-86	-14	-7
17	342	337	3
18	-92	99	-17

-7	8	L	
9	64	20	4
10	349	376	-19
11	90	95	-1
12	422	417	4
13	46	-1	2
14	339	334	3
15	57	1	3
16	277	303	-13
17	61	63	0

-7	9	L	
1	296	266	18
2	48	43	0
3	374	360	9
4	126	76	12
5	467	451	12
6	-90	5	-9
7	353	346	4
8	-69	22	-6
9	324	307	10
10	132	107	6
11	358	369	-6
12	-63	33	-5
13	318	323	-3
14	87	-4	7
15	212	232	-8

-7	10	L	
1	-58	59	-8
2	252	283	-17
3	38	76	-4
4	398	392	4
5	100	93	1
6	414	423	-7
7	-39	75	-8
8	229	267	-18
9	36	45	0
10	251	291	-20
11	-59	63	-7
12	351	362	-6
13	72	42	3

-7	11	L	
1	247	236	5
2	70	0	5
3	326	324	1
4	-50	61	-6
5	317	320	-1
6	91	81	1
7	247	269	-10
8	132	54	15
9	273	294	-11
10	-54	69	-7

-7	12	L	
3	47	-1	2
4	251	262	-4

-6	0	L	
2	853	882	-23
4	834	906	-59
6	756	852	-81
8	727	783	-46
10	722	815	-74
18	499	485	11
20	396	391	3

-6	1	L	
1	513	515	-2
2	206	-176	24
3	1066	1121	-56
4	175	-216	-34
5	911	1044	-153
6	78	109	-12
7	463	511	-57
8	-69	54	-16
9	568	589	-25
17	446	425	16
18	59	10	4
19	472	455	13
20	128	63	13
21	331	307	13

-6	2	L	
1	150	182	-23
2	866	874	-9
3	128	-101	14
4	766	858	-112
5	278	315	-39
6	749	782	-38
7	23	-59	-6
8	664	670	-6
9	208	-193	10
17	98	-115	-4
18	393	368	18
19	-88	11	-8
20	370	346	14
21	155	67	20

-6	3	L	
1	803	865	-71
2	-11	-1	0
3	741	772	-35
4	74	32	10
5	673	681	-9
6	150	111	21
7	807	826	-20
8	88	26	14
17	494	457	29
18	61	-73	-1
19	265	252	6
20	-103	47	-13
21	200	219	-7

-6	4	L	
1	85	-97	-4
2	649	706	-67
3	167	-167	0
4	542	514	31
5	-47	-23	-6
6	830	821	10
16	472	473	0
17	40	-34	0
18	331	315	9
19	47	-29	1
20	267	244	10

-6	5	L	
15	480	474	5
16	117	55	12
17	370	377	-4
18	106	4	12
19	228	227	0
20	99	-49	7

-6	6	L	
14	451	452	0
15	-59	2	-4
16	377	382	-3
17	-82	43	-9
18	233	229	2
19	80	41	4

-6	7	L	
13	396	401	-3
14	108	-59	9
15	390	403	-9
16	108	27	11
17	303	312	-5
18	68	87	-2

-6	8	L	
11	-51	92	-13
12	455	441	11
13	40	16	1
14	368	345	15
15	104	-5	11
16	296	317	-11
17	66	65	0

-6	9	L	
7	400	362	28
8	139	150	-3
9	395	407	-8
10	130	146	-5
11	486	465	16
12	-127	45	-19
13	425	416	6
14	69	5	5
15	233	274	-18
16	-52	59	-6

-6	10	L	
1	-34	32	-2
2	369	371	-1
3	71	92	-4
4	545	539	4
5	135	81	13
6	435	424	8
7	97	26	10
8	312	298	8
9	-109	50	-16
10	350	341	6
11	132	90	9
12	432	421	7
13	58	59	0
14	258	273	-6

-6	11	L	
1	304	305	0
2	-39	28	-2
3	378	396	-12
4	57	56	0
5	356	346	6
6	114	34	13
7	260	260	0
8	-111	-2	-13
9	300	284	8
10	154	20	25
11	326	330	-2
12	-47	-6	-2

-6	12	L	
1	-34	27	-2
2	266	265	0
3	-51	-20	-3
4	355	321	21
5	137	53	16
6	293	289	1
7	-44	93	-10
8	249	258	-4

-5	0	L	
2	902	902	0
4	1373	1522	-97
6	753	798	-39
8	860	923	-51
10	963	1018	-40
18	577	552	21
20	511	470	30
22	277	244	14

-5	1	L	
1	1158	1241	-84
2	203	247	-45
3	1546	1671	-104
4	220	186	30
5	1073	1176	-110
6	378	427	-64
7	683	726	-53
8	53	-100	-16
9	780	785	-5
10	279	-279	0
11	941	927	13
18	-59	-68	-9
19	458	436	15
20	114	61	10
21	309	294	8
22	142	-14	20

-5	2	L	
1	149	-161	-9
2	994	1068	-83
3	188	151	29
4	1022	1070	-51
5	177	196	-15
6	1181	1218	-36
7	66	-42	6
8	691	654	42
9	81	-114	-13
10	760	709	53
18	437	405	23
19	-54	50	-6

20	333	308	14
21	58	37	2

-5 3 L

1	962	1001	-42
2	321	-331	-12
3	845	896	-59
4	-78	44	-21
5	812	878	-78
6	295	327	-35
7	936	886	51
8	108	-105	1
9	1026	1028	-2
17	536	501	28
18	-28	-86	-9
19	365	333	20
20	-87	66	-12
21	282	251	14

-5 4 L

1	308	-311	-3
2	715	773	-70
3	103	-51	19
4	719	709	10
5	361	378	-18
6	1267	1269	-1
7	115	113	0
8	1006	953	50
17	114	-128	-4
18	401	365	24
19	59	-34	2
20	305	274	16
21	61	35	2

-5 5 L

1	790	818	-31
2	110	-150	-21
3	689	763	-88
4	237	238	-1
5	813	791	23
6	106	95	4
16	75	-23	6
17	394	368	18
18	55	34	2
19	277	236	19
20	-60	-37	-4

-5 6 L

15	143	131	3
16	476	464	9
17	118	124	-1
18	175	206	-11
19	-51	17	-3

-5 7 L

14	36	-53	-1
15	464	461	2
16	58	60	0
17	311	319	-4
18	-65	62	-8
19	259	243	7

-5 8 L

12	457	436	16
13	-14	-54	-3
14	384	384	0
15	-103	57	-14
16	342	325	9
17	130	79	10
18	303	310	-3

-5 9 L

9	422	423	-1
10	52	106	-10
11	486	485	0
12	-108	4	-13
13	420	413	5
14	62	48	1
15	279	263	8
16	156	90	16

-5 10 L

1	80	59	3
2	609	593	13
3	104	89	3
4	594	592	1
5	106	46	11
6	440	434	4
7	-96	52	-15
8	312	299	8
9	107	45	11
10	389	381	5
11	-33	59	-5
12	384	386	-1
13	-78	4	-6
14	247	246	0
15	-130	-30	-17

-5 11 L

1	313	337	-15
2	59	55	0
3	443	465	-16
4	116	107	2
5	412	417	-3
6	73	49	3
7	282	271	6
8	103	-33	11
9	373	372	1
10	37	-7	1
11	358	346	7
12	-83	16	-7
13	155	183	-8

-5 12 L

1	102	18	11
2	318	316	1
3	-91	21	-9
4	333	324	5
5	-21	70	-5
6	289	292	-1
7	-102	40	-12
8	295	282	6
9	97	-30	8
10	265	258	3

-5 13 L

1	252	282	-13
2	-15	4	0
3	293	304	-5
4	93	72	3

-4 0 L

2	1705	1789	-46
4	1540	1633	-55
6	1054	1169	-90
8	1401	1396	2
10	1261	1299	-24
18	643	601	35
20	340	324	10
22	192	225	-12

-4 1 L

1	1188	1274	-89
2	18	-48	-6
3	1348	1452	-98
4	459	546	-136
5	1275	1394	-117
6	320	333	-16
7	581	590	-12
8	-30	61	-11
9	1070	1120	-51
10	115	-113	0
11	1024	981	41
18	-60	-75	-11
19	489	427	45
20	36	11	1
21	276	246	15
22	-74	-61	-9

-4 2 L

1	367	-417	-74
2	889	968	-98
3	-51	15	-8
4	1087	1098	-12
5	136	-124	8
6	628	661	-43
7	258	-253	4
8	770	802	-38
9	85	-129	-21
10	909	867	42
11	107	107	0
18	457	382	55
19	-78	66	-11
20	359	302	34
21	-26	85	-8

-4 3 L

1	586	644	-81
2	54	-62	-2
3	778	886	-142
4	340	308	39
5	637	632	5
6	144	-95	28
7	1409	1415	-5
8	284	-223	54
9	868	821	48
10	40	-52	-2
17	423	393	23
18	78	49	4
19	325	306	10
20	134	106	7
21	315	262	25

-4 4 L

1	153	99	32
2	571	593	-30
3	-61	64	-21
4	685	722	-46
5	196	207	-9
6	1272	1226	40
7	192	190	1
8	1057	1014	40
9	-69	-41	-13
17	120	-130	-3
18	376	328	31
19	-29	8	-1
20	402	347	34
21	109	-23	11

-4 5 L

1	915	925	-11
2	181	-170	8
3	774	796	-26
4	-4	38	-3
5	1039	1022	16
6	221	191	23
7	970	924	44
8	164	-132	17
16	77	-51	4
17	479	450	22
18	25	18	0
19	370	330	24
20	147	-52	18

-4 6 L

1	135	178	-27
2	755	789	-38
3	61	27	6
4	787	821	-37
5	230	-219	8
15	45	109	-11
16	459	429	22
17	-89	59	-13
18	218	243	-11
19	-104	-4	-10
20	292	282	4

-4 7 L

14	-47	-33	-4
15	422	415	4
16	58	64	0
17	322	307	8
18	-117	20	-14
19	258	253	2

-4 8 L

13	151	-102	14
14	440	417	17
15	93	41	7
16	311	344	-20
17	-65	48	-6
18	265	317	-25

-4 9 L

10	62	-50	1
11	526	544	-15
12	133	-91	11
13	346	353	-4
14	47	-8	2
15	276	270	2
16	-49	41	-4

-4 10 L

7	53	82	-5
8	383	384	0
9	0	43	-2
10	460	443	12
11	92	49	6
12	383	379	2
13	123	-12	16
14	244	232	5
15	35	-28	0

-4 11 L

1	385	397	-8
2	73	17	6
3	532	529	1
4	125	92	8
5	380	392	-9
6	62	24	3
7	340	315	16
8	38	-54	-1
9	394	397	-2
10	-113	33	-14
11	350	352	-1
12	152	48	21
13	190	195	-1

-4 12 L

1	-113	10	-14
2	301	310	-4
3	-69	64	-9
4	347	324	14
5	-67	97	-14
6	287	297	-5
7	-48	24	-3
8	281	297	-8
9	64	-30	3
10	298	317	-10
11	57	2	3

-4 13 L

1	227	237	-4
2	-60	-10	-4
3	285	283	0
4	88	98	-1
5	310	314	-1
6	-22	74	-5
7	261	286	-12

-3 0 L

2	1313	1552	-174
4	445	470	-27
6	1021	1021	0
8	1215	1219	-2
10	1240	1235	3
12	680	638	31
18	536	504	25
20	307	299	4
22	146	167	-6

-3 1 L

1	948	1020	-89
2	568	633	-101
3	1621	1733	-92
4	45	-14	5
5	691	684	9
6	55	-51	1
7	446	483	-52
8	516	-467	61
9	1011	999	12
10	111	-121	-5
11	1069	1040	27

12	77	-39	8
18	-63	37	-6
19	419	390	20
20	-49	6	-2
21	228	219	3
22	-67	-41	-5

-3 2 L

1	610	-682	-111
2	1368	1398	-27
3	100	127	-18
4	765	756	11
5	57	37	5
6	1012	1008	3
7	626	-545	98
8	843	820	25
9	47	-98	-17
10	640	630	11
11	222	216	4
18	461	421	31
19	126	106	4
20	316	294	12
21	-34	12	-1

-3 3 L

1	938	995	-68
2	68	67	0
3	834	857	-29
4	316	291	31
5	1034	1036	-1
6	196	-119	55
7	915	860	59
8	464	-419	51
9	892	893	0
10	153	156	-1
11	786	726	62
18	115	76	9
19	349	302	28
20	85	100	-3
21	289	250	19

-3 4 L

1	95	53	18
2	192	194	-1
3	109	127	-11
4	577	628	-70
5	664	631	40
6	1043	918	171
7	179	119	38
8	992	946	46
9	94	-99	-1
10	632	560	75
17	82	1	8
18	320	266	32
19	-51	108	-16
20	343	321	12
21	-113	26	-13

-3 5 L

1	467	504	-47
2	103	-106	-1
3	751	721	35
4	313	356	-52
5	1129	1168	-38
6	89	29	17
7	911	796	113
8	206	175	21
9	511	478	35
16	-67	-67	-10
17	319	301	11
18	109	-8	13
19	300	286	7
20	-167	-32	-28

-3 6 L

1	184	201	-13
2	664	612	59
3	245	-243	1
4	813	791	24
5	210	-160	35
6	1014	1011	2
7	-81	20	-14
15	59	66	-1
16	382	397	-11
17	85	-19	7
18	250	242	4
19	120	-93	5
20	341	316	13

-3 7 L

1	455	394	62
2	120	151	-17
3	669	695	-29
14	162	145	6
15	385	386	0
16	109	115	-1
17	303	280	12
18	-88	-2	-7
19	262	275	-5

-3 8 L

13	116	-35	15
14	343	350	-4
15	52	99	-8
16	323	315	4
17	78	0	6
18	277	262	7

-3 9 L

11	477	474	2
12	102	-94	1
13	327	347	-13
14	-79	0	-7
15	297	284	7
16	95	-15	9
17	261	273	-5

-3 10 L

8	419	397	17
9	55	38	2
10	434	451	-12
11	-134	-16	-20
12	364	360	3
13	151	-28	25
14	325	274	28
15	-65	-34	-5

-3 11 L

1	489	475	11
2	-110	33	-16
3	470	486	-12
4	83	57	4
5	348	373	-17
6	34	-41	0
7	348	331	11
8	110	-48	11
9	413	416	-2
10	70	16	5
11	307	315	-4
12	67	91	-4
13	168	194	-9

-3 12 L

1	-65	13	-4
2	376	389	-8
3	143	77	17
4	349	335	9
5	116	14	15
6	277	298	-11
7	109	-31	12
8	338	336	1
9	43	-38	0
10	332	336	-2
11	-95	43	-11

-3 13 L

1	245	259	-6
2	61	-15	3
3	244	247	-1
4	152	91	16
5	254	244	4
6	-47	-3	-2
7	236	230	2
8	133	-55	15

-2 0 L

2	1009	1106	-85
4	989	1050	-52
6	800	772	25
8	625	610	13
10	796	741	43
12	249	256	-3
18	539	517	18
20	261	235	12

-2 1 L

1	1438	1596	-149
2	896	-836	72
3	1351	1370	-18
4	660	602	79
5	763	718	59
6	390	-413	-33
7	736	714	28
8	247	-218	29
9	1285	1209	66
10	-34	-14	-3
11	745	695	54
12	33	-26	0
18	-57	30	-5
19	357	316	27
20	29	22	0
21	273	228	22

-2 2 L

1	677	-730	-79
2	836	901	-86
3	1392	1279	97
4	1391	1251	118
5	396	-335	81
6	1082	1018	66
7	304	-294	12
8	1180	1086	86
9	56	64	-2
10	882	849	35
11	202	218	-13
18	410	382	20
19	76	71	0
20	301	278	13
21	49	-32	1

-2 3 L

1	901	894	9
2	229	158	71
3	1231	1231	0
4	85	90	-2
5	900	759	152
6	511	-434	95
7	1162	1104	55
8	324	-249	76
9	945	856	89
10	111	117	-3
11	734	656	81
17	341	317	16
18	49	9	2
19	335	330	2
20	30	9	0
21	269	260	4

-2 4 L

1	319	-274	56
2	546	491	73
3	-37	-47	-11
4	674	720	-62
5	108	120	-7
6	1302	1245	50
7	208	-175	25
8	755	686	75
9	196	166	21
10	646	607	42
17	112	-73	9
18	263	229	17
19	-141	37	-23
20	335	315	11
21	15	-26	0

-2 5 L

1	791	767	28
2	162	156	4
3	1195	1134	56
4	84	43	13
5	1108	1075	32
6	443	351	99
7	706	615	98
8	189	125	39
9	417	419	-1
16	-43	-13	-2
17	282	280	0
18	115	61	10
19	308	265	24
20	-38	-5	-1

-2 6 L

1	306	240	62
2	785	745	45
3	65	-22	8
4	1085	997	82
5	36	-42	0
6	985	892	89
7	-29	49	-7
15	167	133	12
16	357	381	-17
17	-50	-8	-3
18	361	323	24
19	143	-60	17

-2 7 L

1	723	666	60
2	250	-157	66
3	666	596	74
4	206	-135	44
14	78	111	-7
15	287	302	-9
16	-100	49	-13
17	326	318	5
18	30	-43	-1
19	264	278	-6

-2 8 L

13	51	-15	3
14	329	338	-5
15	151	135	5
16	284	288	-2
17	123	2	16
18	221	208	4

-2 9 L

11	437	437	0
12	-46	-32	-4
13	293	271	12
14	-87	36	-10
15	214	286	-51
16	-31	0	0

-2 10 L

8	434	432	0
9	107	-3	14
10	386	391	-3
11	-45	-63	-7
12	260	251	4
13	88	-29	7
14	271	260	4
15	103	-45	8

-2 11 L

3	534	536	-1
4	74	29	6
5	393	394	0
6	77	-1	7
7	344	357	-8
8	117	-68	10
9	377	379	-1
10	108	50	10
11	254	284	-15
12	57	64	0
13	227	213	6

-2 12 L

1	82	55	4
2	387	391	-2
3	126	77	11
4	307	313	-4
5	-29	-3	0
6	350	346	2
7	195	-113	28
8	359	357	1

9	108	-41	10
10	322	313	5
11	27	20	0

-2 13 L

1	228	251	-10
2	40	10	1
3	293	290	1
4	172	74	26
5	281	307	-13
6	76	-46	3
7	233	230	1
8	123	-68	10

-1 0 L

2	2224	2239	-6
4	296	-155	109
6	907	888	16
8	1366	1266	60
10	784	715	53
12	336	318	12
18	346	341	3
20	192	187	2

-1 1 L

1	1233	1173	61
2	-31	-100	-47
3	1370	1226	128
4	322	-289	45
5	1143	1015	127
6	701	-624	98
7	1473	1374	80
8	182	-176	5
9	1094	1001	89
10	280	251	28
11	863	797	67
18	187	132	20
19	321	308	8
20	60	-16	3
21	271	215	26

-1 2 L

1	970	848	137
2	1613	1524	70
3	318	321	-4
4	1064	986	84
5	66	60	2
6	1195	1087	102
7	486	-429	73
8	1311	1208	89
9	190	197	-6
10	929	864	66
11	282	258	20
18	317	316	0
19	179	35	37
20	226	229	-1
21	-56	-91	-12

-1 3 L

1	1549	1381	131
2	528	499	42
3	1281	1061	192
4	503	428	102
5	1146	1078	67
6	342	-333	11
7	828	769	67
8	308	-271	39
9	929	907	23
10	389	342	48
11	726	662	66
17	330	311	12
18	49	-12	2
19	299	240	32
20	75	-66	1
21	230	225	1

-1 4 L

1	521	441	105
2	1116	1031	85
3	265	190	76
4	1994	1661	200
5	293	-221	76
6	1139	1047	87
7	-59	-40	-13
8	1022	947	74
9	12	-38	-2
10	919	833	83
17	0	13	0
18	342	328	8
19	-122	3	-15
20	373	356	10

-1 5 L

1	1109	976	128
2	256	191	62
3	1807	1477	211
4	201	150	40
5	1790	1522	174
6	178	182	-2
7	896	839	59
8	22	-12	0
9	544	490	57
16	111	113	0
17	362	363	0
18	102	82	4
19	388	365	14
20	-159	29	-24

-1 6 L

1	26	9	1
2	941	757	178
3	235	-194	35
4	1165	978	162
5	41	-78	-9
6	1172	1031	123
7	288	246	38
15	110	85	6
16	301	312	-6
17	74	-74	0
18	339	315	13
19	-86	-34	-8

-1 7 L

1	681	555	131
2	468	-397	75
3	1113	915	171
4	-42	-24	-4
5	1049	904	130
14	45	91	-7
15	287	294	-4
16	60	-9	4
17	317	289	16
18	-34	-86	-8

-1 8 L

13	-24	20	-1
14	379	368	7
15	48	83	-5
16	299	315	-8
17	69	-60	1

-1 9 L

11	365	357	5
12	20	-31	0
13	223	273	-26
14	85	14	7
15	315	290	14
16	144	-66	16

-1 10 L

8	525	523	2
9	-50	27	-3
10	375	371	2
11	73	-64	1
12	261	240	10
13	-30	-26	-1
14	273	275	-1
15	-101	-22	-10

-1 11 L

4	114	63	11
5	322	331	-5
6	-85	-61	-13
7	453	441	10
8	137	-33	21
9	358	378	-13
10	-63	31	-5
11	242	245	-1
12	-46	39	-4
13	189	231	-16

-1 12 L

1	100	54	8
2	369	373	-2
3	105	66	8
4	320	330	-6
5	138	-80	13
6	379	374	3
7	63	-68	0
8	336	363	-16
9	-111	3	-12
10	254	296	-20
11	-55	22	-3

-1 13 L

1	280	303	-13
2	118	77	8
3	268	318	-27
4	34	62	-2
5	303	303	0
6	118	-56	11
7	246	284	-18
8	115	-40	11

-1 14 L

1	-78	30	-7

0 0 L

2	2288	2362	-45
4	1458	1361	82
6	1664	1492	126
8	1324	1214	95
10	648	581	76
12	582	603	-17
14	740	766	-19
16	563	565	-1
18	307	308	-1
20	248	236	8

0 1 L

1	2144	1818	272
2	515	-393	266
3	1872	1751	117
4	289	232	99
5	1405	1304	123
6	422	-404	35
7	1224	1146	104
8	171	158	14
9	1207	1109	124
10	42	92	-22
11	710	650	89
12	57	69	-2
13	531	536	-4
14	-38	-121	-19
15	611	590	14
16	128	141	-3
17	499	480	24
18	151	96	23
19	282	257	19
20	79	16	9
21	225	213	7

0 2 L

0	844	707	170
1	196	167	47
2	1153	968	255
3	972	863	170
4	762	638	217
5	148	-131	20
6	1571	1526	50
7	435	-373	109
8	1336	1246	108
9	237	237	-1
10	813	764	73
11	65	121	-31
12	627	638	-8
13	138	-176	-15
14	639	660	-22
15	101	57	8
16	465	459	4
17	146	134	6
18	272	254	14
19	79	-10	10
20	212	207	2

0 3 L

1	1783	1391	365
2	1034	827	298
3	2093	1842	210
4	153	115	42
5	1761	1491	273
6	128	-91	31
7	918	844	112
8	292	236	78
9	1071	1040	42
10	276	278	-2
11	799	837	-30
12	64	-6	5
13	535	546	-9
14	191	-158	13
15	451	472	-14
16	-128	-16	-17
17	323	302	19
18	88	9	13
19	277	257	15
20	91	-58	7

0 4 L

0	1107	899	199
1	74	98	-18
2	1850	1475	336
3	389	327	112
4	1603	1397	213
5	103	57	29
6	1383	1244	161
7	94	35	27
8	868	805	94
9	204	204	0
10	782	849	-56
11	100	-84	6
12	697	758	-49
13	-83	-110	-22
14	402	414	-8
15	65	-100	-6
16	312	302	10
17	64	41	4
18	399	396	2
19	-38	24	-3
20	359	352	6

0 5 L

1	991	791	279
2	137	88	40
3	1651	1391	257
4	97	-86	7
5	1181	1009	216
6	175	-193	-20
7	696	628	107
8	-93	13	-29
9	630	696	-57
10	35	-9	1
11	885	941	-43
12	272	-260	6
13	606	648	-32
14	98	31	9
15	361	373	-7
16	-28	22	-2
17	353	366	-13
18	116	34	19
19	368	351	14

0 6 L

0	1297	1038	209
1	207	-164	47
2	1107	942	213
3	443	-373	109
4	1362	1121	266
5	147	95	37
6	890	772	164
7	88	76	6
8	609	617	-6
9	167	-161	2
10	508	543	-28
11	71	0	6
12	648	701	-40
13	154	87	18
14	407	467	-39

15	84	-9	13
16	267	286	-15
17	120	-74	14
18	303	313	-8
19	48	-29	2

Ø 7 L

1	853	696	218
2	172	-119	44
3	1209	1035	206
4	131	127	2
5	971	883	62
6	130	56	19
7	631	625	4
8	122	-105	5
9	559	589	-23
10	166	-209	-19
11	473	541	-51
12	84	77	1
13	358	373	-9
14	119	51	21
15	225	238	-9
16	82	-37	9
17	319	304	12
18	58	-89	-6

Ø 8 L

Ø	999	915	58
1	237	-232	2
2	876	786	65
3	211	-150	27
4	674	604	53
5	86	27	8
6	747	708	28
7	-49	-60	-7
8	696	717	-15
9	248	-221	12
10	573	604	-22
11	93	-98	-1
12	395	409	-17
13	-25	28	-2
14	325	333	-7
15	111	13	20
16	299	290	7
17	72	-91	-4

Ø 9 L

1	833	784	35
2	305	-271	18
3	742	721	15
4	168	-170	Ø
5	661	632	21
6	-43	87	-10
7	793	761	21
8	29	-39	Ø
9	615	637	-15
10	134	-67	14
11	362	391	-32
12	59	45	2
13	314	338	-23
14	37	-5	2
15	312	317	-4
16	83	-67	3

Ø 10 L

Ø	709	683	18
1	-76	52	-9
2	686	659	18
3	151	66	20
4	522	501	13
5	54	33	1
6	577	553	16
7	109	43	10
8	539	543	-5
9	-40	15	-3
10	339	349	-9
11	64	-14	7
12	204	223	-13
13	68	-8	7
14	292	307	-12

Ø 11 L

1	654	662	-5
2	117	119	Ø
3	349	346	1
4	-44	7	-4
5	355	367	-12
6	-6	-12	Ø
7	415	416	-1
8	43	-17	2
9	284	299	-13
10	102	22	16
11	207	239	-21
12	72	-12	7
13	220	244	-15

Ø 12 L

Ø	516	531	-12
1	106	51	14
2	436	448	-14
3	-99	5	-16
4	367	382	-14
5	91	-77	3
6	366	366	Ø
7	110	-65	12
8	332	351	-16
9	-105	47	-19
10	235	253	-11
11	31	30	Ø

Ø 13 L

1	347	360	-11
2	-79	45	-12
3	358	352	5
4	-125	11	-22
5	344	347	-2
6	-92	-67	-18
7	258	289	-20
8	19	Ø	Ø

Ø 14 L

Ø	174	189	-5
1	101	33	13
2	165	233	-34

1 Ø L

Ø	1877	2368	-288
2	1587	1540	26
4	1145	1058	62
6	1769	1709	60
8	1662	1557	53
10	685	612	56
12	674	687	-10
14	752	739	9
16	424	430	-4
18	302	292	6
20	271	271	Ø

1 1 L

Ø	486	-527	-79
1	1807	1888	-61
2	1457	-1480	-20
3	1406	1296	96
4	1434	-1331	88
5	1386	1352	29
6	200	-191	9
7	1587	1518	52
8	-30	-20	-3
9	881	820	66
10	168	175	-5
11	537	529	7
12	25	-12	Ø
13	587	576	8
14	61	-121	-12
15	609	606	2
16	70	35	3
17	338	361	-16
18	-54	24	-4
19	265	256	5
20	80	-49	4

1 2 L

Ø	1354	1293	55
1	913	850	75
2	875	847	34
3	338	-359	-32
4	1318	1269	45
5	664	-569	120
6	1386	1337	43
7	194	-189	4
8	997	948	50
9	441	413	32
10	807	770	38
11	-76	5	-8
12	608	619	-9
13	53	-73	-3
14	561	545	11
15	-41	54	-5
16	444	422	13
17	99	126	-7
18	273	239	17
19	74	-72	Ø
20	241	190	22

1 3 L

Ø	82	126	-30
1	958	846	124
2	178	127	43
3	1685	1612	54
4	-35	-39	-8
5	1057	1039	19
6	-83	33	-23
7	1110	1063	46
8	154	154	Ø
9	1186	1118	60
10	137	152	-9
11	732	750	-15
12	114	-100	3
13	631	640	-7
14	-138	-46	-25
15	362	348	8
16	42	51	-1
17	306	313	-4
18	-55	24	-4
19	234	226	3
20	65	-28	3

1 4 L

Ø	1241	1134	99
1	209	194	14
2	1713	1485	159
3	306	299	8
4	1490	1401	71
5	532	-525	9
6	720	672	57
7	142	80	33
8	623	549	83
9	-67	21	-13
10	750	779	-23
11	-83	-27	-10
12	629	648	-14
13	142	-189	-17
14	297	312	-8
15	-112	38	-15
16	342	337	4
17	43	32	1
18	380	366	9
19	-31	-23	-1

1 5 L

Ø	103	64	17
1	1336	1169	140
2	131	143	-7
3	1312	1155	132
4	332	-272	66
5	887	783	108
6	53	17	6
7	402	357	48
8	51	Ø	7
9	551	577	-22
10	124	-153	-11
11	661	699	-30
12	-69	-47	-8
13	415	441	-18
14	Ø	-26	Ø
15	299	323	-17
16	102	5	13
17	327	332	-3
18	-109	-19	-13
19	331	314	10

1 6 L

Ø	1070	855	196
1	475	-391	95
2	1158	996	144
3	-38	-34	-6
4	1075	982	87
5	136	103	16
6	920	837	82
7	37	-20	1
8	555	600	-39
9	-31	-30	-2
10	623	671	-38
11	55	-54	Ø
12	495	548	-39
13	-142	-14	-24
14	363	374	-11
15	73	-53	3
16	304	311	-4
17	146	-95	14
18	310	300	5

1 7 L

Ø	-37	5	-3
1	1029	875	142
2	292	-241	43
3	1058	970	81
4	152	146	4
5	889	836	39
6	115	140	-8
7	612	613	Ø
8	275	-234	23
9	531	553	-17
10	96	-132	-9
11	536	594	-42
12	21	133	-19
13	298	337	-35
14	-31	11	-1
15	270	286	-9
16	143	-103	11
17	301	290	5

1 8 L

Ø	1074	970	69
1	96	51	8
2	828	742	63
3	-86	33	-11
4	536	470	49
5	192	177	6
6	503	487	11
7	101	-58	7
8	618	612	4
9	56	-73	-2
10	462	511	-35
11	-121	-14	-16
12	356	374	-14
13	102	76	5
14	364	371	-5
15	42	-18	1
16	255	262	-3

1 9 L

Ø	64	-28	4
1	613	586	20
2	282	-252	16
3	565	543	15
4	125	93	8
5	694	686	6
6	68	132	-14
7	625	622	2
8	107	-125	-4
9	526	546	-14
10	73	-79	-1
11	347	398	-41
12	-54	9	-4
13	349	356	-5
14	-50	-34	-4
15	288	312	-13

1 10 L

Ø	649	605	30
1	-20	-7	Ø
2	504	479	16
3	152	90	16
4	552	539	8
5	130	-153	-6
6	680	684	-2
7	120	-97	4
8	590	602	-10
9	99	-76	5
10	307	332	-17

11	88	-92	0
12	246	265	-10
13	99	-67	6
14	288	311	-13

1 11 L

0	75	27	4
1	508	496	7
2	60	32	2
3	367	358	8
4	-64	16	-7
5	417	407	7
6	65	-58	0
7	455	455	0
8	98	-36	9
9	252	299	-26
10	-30	-15	-1
11	182	217	-15
12	75	-42	4

1 12 L

0	454	465	-8
1	-159	11	-28
2	374	406	-23
3	-86	-44	-10
4	306	323	-10
5	-36	-104	-13
6	344	352	-5
7	83	-19	7
8	279	295	-8
9	-78	53	-9
10	162	213	-19

1 13 L

0	-56	-27	-4
1	296	302	-3
2	-50	-51	-5
3	379	346	21
4	129	-157	-8
5	336	333	1
6	89	-115	-5
7	255	274	-9

1 14 L

0	192	226	-13

2 0 L

0	1788	1991	-112
2	256	-231	22
4	676	-642	33
6	553	533	18
8	851	802	38
10	316	323	-7
12	674	697	-18
14	644	633	7

16	403	389	11
18	151	163	-4

2 1 L

0	142	81	45
1	885	863	28
2	216	225	-12
3	571	620	-76
4	150	-204	-56
5	1288	1288	0
6	59	-20	8
7	780	795	-18
8	-65	54	-18
9	621	552	77
10	-23	4	-1
11	564	578	-11
12	114	-104	2
13	624	622	1
14	100	-59	7
15	502	474	18
16	13	36	-1
17	264	289	-14
18	-36	-12	-1
19	232	226	2

2 2 L

0	1071	1108	-42
1	511	476	52
2	1362	1366	-3
3	751	-714	47
4	1142	1079	63
5	811	-770	49
6	1471	1450	17
7	118	-122	-2
8	1049	1030	18
9	58	81	-6
10	651	667	-13
11	77	-81	0
12	414	457	-32
13	67	-78	-2
14	514	507	4
15	129	120	2
16	326	337	-8
17	76	35	5
18	245	233	5
19	159	-96	17

2 3 L

0	354	305	66
1	415	406	13
2	35	90	-21
3	945	921	26
4	117	-70	25
5	1054	1032	22
6	220	-157	51
7	894	851	46
8	-83	-4	-15

9	712	694	24
10	85	-117	-8
11	723	738	-12
12	180	-200	-8
13	408	423	-10
14	104	-42	11
15	310	306	4
16	-75	76	-14
17	313	289	15
18	-110	-4	-14
19	258	232	12

2 4 L

0	958	900	63
1	541	560	-26
2	1455	1420	28
3	132	81	27
4	1069	1050	19
5	-31	-69	-15
6	467	454	16
7	109	73	15
8	573	539	38
9	-68	48	-10
10	739	789	-40
11	260	-258	1
12	400	419	-13
13	142	-144	0
14	320	329	-5
15	-39	28	-3
16	325	306	12
17	-96	-14	-11
18	316	294	12
19	31	-28	0

2 5 L

0	68	51	5
1	1236	1167	63
2	296	-279	18
3	1236	1176	53
4	94	-32	19
5	691	694	-3
6	198	-190	6
7	509	500	12
8	66	35	4
9	601	653	-44
10	32	78	-6
11	578	597	-14
12	52	-75	-3
13	270	306	-19
14	25	2	1
15	188	215	-13
16	-65	-15	-5
17	293	296	-1
18	-58	-25	-4

2 6 L

0	1047	919	122

1	358	-346	13
2	1141	1091	46
3	156	-164	-5
4	864	774	91
5	118	73	18
6	489	494	-4
7	58	-29	3
8	717	753	-29
9	130	-85	13
10	438	480	-31
11	93	-19	10
12	416	452	-25
13	82	75	1
14	292	284	5
15	25	-55	-3
16	294	302	-4
17	-84	-56	-10

2 7 L

0	154	-109	23
1	771	702	71
2	72	32	10
3	1083	1003	54
4	227	222	3
5	715	676	30
6	-105	69	-22
7	443	462	-14
8	304	-311	-4
9	570	616	-35
10	-90	-36	-11
11	432	471	-27
12	81	126	-16
13	303	338	-24
14	-98	-24	-13
15	322	308	8
16	59	-73	-2
17	273	296	-12

2 8 L

0	732	659	54
1	177	-150	11
2	562	518	33
3	31	40	0
4	526	479	34
5	109	55	11
6	627	607	15
7	61	5	4
8	523	530	-5
9	-35	-81	-9
10	406	403	1
11	-97	62	-18
12	268	318	-32
13	-113	72	-22
14	279	292	-8
15	-119	-47	-18
16	188	213	-10

2 9 L

0	422	-404	12
1	370	349	13
2	189	-235	-20
3	427	410	11
4	27	68	-4
5	517	485	22
6	75	13	6
7	484	470	9
8	-89	-35	-9
9	305	322	-15
10	-59	13	-5
11	232	263	-17
12	-14	35	-1
13	274	276	-1
14	111	-76	7

2 10 L

0	498	474	15
1	-60	83	-11
2	351	329	12
3	98	-33	9
4	430	398	19
5	126	-90	8
6	561	531	19
7	93	-70	4
8	391	394	-2
9	-20	-53	-4
10	248	258	-5
11	77	-55	3
12	270	260	5
13	-77	-92	-15

2 11 L

0	116	14	13
1	422	420	1
2	98	47	12
3	262	254	4
4	77	-22	7
5	370	389	-13
6	-113	-70	-20
7	419	416	1
8	138	-48	20
9	241	272	-16
10	-99	-82	-18
11	232	251	-8

2 12 L

0	395	417	-16
1	93	-16	9
2	290	304	-8
3	154	-81	20
4	270	288	-10
5	120	-118	0
6	258	251	3
7	100	-26	10
8	31	205	-40

9	67	13	4

2 13 L

0	74	77	0
1	272	291	-9
2	136	-46	17
3	326	295	17
4	229	-157	28
5	237	256	-8
6	-90	-70	-13

3 0 L

0	1025	1089	-52
2	555	573	-19
4	465	457	7
6	1195	1188	4
8	371	368	2
10	194	193	0
12	484	492	-5
14	535	532	2
16	206	214	-3
18	187	176	4

3 1 L

0	288	305	-24
1	731	848	-171
2	103	-204	-98
3	1136	1162	-26
4	97	-92	2
5	787	812	-30
6	634	628	7
7	479	470	11
8	427	387	44
9	430	439	-12
10	212	208	1
11	396	404	-5
12	-85	26	-10
13	496	512	-11
14	-107	23	-13
15	343	356	-12
16	-53	14	-3
17	251	226	13
18	30	-12	0
19	196	195	0

3 2 L

0	1436	1496	-53
1	149	132	14
2	486	533	-71
3	414	-404	13
4	1052	1094	-45
5	344	-352	-10
6	959	966	-7
7	221	191	24
8	722	726	-4
9	159	147	5

10	424	435	-8
11	207	-219	-5
12	430	451	-15
13	20	-16	0
14	402	387	9
15	-100	11	-13
16	260	249	6
17	0	-14	0
18	223	208	6

3 3 L

0	265	280	-19
1	449	508	-89
2	257	249	9
3	1035	1031	4
4	179	-195	-14
5	801	822	-23
6	96	35	19
7	806	755	55
8	42	35	1
9	638	691	-44
10	323	-312	7
11	596	609	-9
12	211	-202	3
13	306	293	7
14	-131	5	-19
15	249	271	-13
16	-46	36	-4
17	271	253	9
18	-86	-55	-11

3 4 L

0	860	927	-81
1	138	107	19
2	1134	1131	3
3	255	167	77
4	533	534	-1
5	116	107	5
6	335	342	-8
7	175	178	-2
8	628	648	-17
9	78	-3	8
10	589	631	-33
11	69	-65	0
12	489	506	-12
13	108	-88	4
14	286	302	-11
15	101	42	11
16	322	307	9
17	-73	-31	-7
18	224	242	-8

3 5 L

0	173	156	12
1	943	907	37
2	103	111	-3
3	812	791	22
4	171	-173	-1
5	539	535	5
6	76	-40	11
7	435	439	-3
8	43	110	-14
9	691	734	-34
10	112	-44	13
11	456	482	-18
12	-71	-34	-7
13	244	281	-30
14	-160	-20	-32
15	275	287	-7
16	-92	-20	-10
17	293	287	3

3 6 L

0	852	834	19
1	260	-290	-29
2	989	962	26
3	16	95	-18
4	585	565	27
5	34	25	0
6	652	652	0
7	155	-158	-1
8	573	584	-8
9	188	-182	3
10	466	507	-29
11	-29	38	-2
12	244	274	-24
13	-34	0	-1
14	251	255	-1
15	-54	-58	-7
16	284	287	-1
17	-31	-2	-1

3 7 L

0	334	-308	30
1	866	788	58
2	202	-192	4
3	695	660	28
4	85	-5	10
5	489	450	28
6	134	-99	10
7	461	478	-12
8	144	-156	-4
9	495	493	2
10	97	6	11
11	366	407	-43
12	77	74	0
13	260	282	-13
14	99	-10	12
15	263	266	-1
16	-124	-73	-22

3 8 L

0	609	564	34
1	215	-246	-15
2	385	344	27
3	124	-83	11
4	443	391	35
5	79	-40	5
6	490	490	0
7	222	-235	-6
8	441	440	0
9	46	-54	0
10	359	377	-14
11	105	42	12
12	308	302	3
13	61	-13	4
14	256	262	-3
15	109	-92	3

3 9 L

0	-69	-42	-7
1	418	403	10
2	130	-9	20
3	465	453	8
4	-74	19	-6
5	538	515	15
6	124	-71	11
7	426	417	5
8	157	-153	2
9	206	223	-9
10	-104	-29	-14
11	233	252	-10
12	-58	0	-3
13	232	240	-4
14	86	-78	1

3 10 L

0	495	453	27
1	-112	56	-17
2	380	355	14
3	96	75	3
4	487	454	20
5	119	-76	14
6	432	424	6
7	53	-77	-3
8	262	275	-7
9	119	30	17
10	183	162	8
11	-57	-20	-4
12	189	201	-4

3 11 L

0	13	19	0
1	283	290	-4
2	101	-17	12
3	269	252	9
4	-37	-42	-3
5	395	405	-7
6	41	-30	0
7	307	316	-5
8	45	-36	0
9	161	179	-6
10	84	-69	2

3 12 L

0	355	356	0
1	0	-14	0
2	402	394	5
3	123	-85	9
4	273	300	-14
5	21	-67	-4
6	193	230	-15
7	71	0	5
8	188	201	-5

3 13 L

0	109	69	7
1	277	273	1
2	69	-70	0
3	272	287	-7
4	50	-114	-10
5	257	262	-2

4 0 L

0	469	490	-21
2	657	764	-107
4	954	1040	-70
6	941	946	-4
8	570	583	-11
10	519	525	-4
12	647	632	10
14	425	430	-4
16	190	204	-6
18	158	163	-1

4 1 L

0	180	159	19
1	925	996	-84
2	193	-260	-78
3	850	886	-43
4	240	-222	17
5	930	942	-13
6	37	62	-5
7	748	733	16
8	102	36	13
9	417	415	1
10	41	75	-5
11	509	522	-9
12	-82	38	-9
13	437	448	-7
14	127	108	7
15	214	245	-16
16	20	0	0
17	130	168	-11
18	-107	-13	-11

4 2 L

0	914	928	-16
1	134	143	-6
2	946	982	-40
3	352	-399	-62
4	974	1032	-63
5	184	-147	26
6	855	864	-10
7	447	446	1
8	503	540	-31
9	71	71	0
10	391	386	3
11	-101	-14	-13
12	313	338	-14
13	-91	28	-10
14	234	237	-1
15	-52	82	-11
16	234	206	13
17	-46	-60	-6

4 3 L

0	203	252	-53
1	782	795	-15
2	456	-440	20
3	680	711	-38
4	-55	-54	-15
5	838	863	-27
6	184	193	-7
7	640	696	-48
8	113	-93	5
9	508	546	-30
10	99	-153	-17
11	452	428	16
12	108	-49	11
13	304	310	-3
14	123	85	10
15	297	261	21
16	94	26	10
17	242	215	12

4 4 L

0	1049	1136	-92
1	-30	-77	-17
2	1032	1048	-16
3	235	-251	-15
4	560	582	-27
5	-63	-30	-11
6	389	403	-10
7	136	-75	18
8	566	580	-11
9	-56	9	-4
10	631	652	-15
11	88	-142	-14
12	334	341	-4
13	76	-7	7
14	291	303	-7
15	36	50	-1
16	279	295	-8
17	98	-9	10

4 5 L

0	197	169	20
1	982	974	8
2	127	-129	-1
3	785	764	22
4	56	-5	8
5	399	408	-7
6	70	94	-5
7	544	543	0
8	67	77	-1
9	535	572	-28
10	-48	-30	-4
11	313	336	-13
12	-72	-4	-9
13	278	264	8
14	-118	-61	-22
15	278	282	-2
16	95	-52	6

4 6 L

0	799	835	-40
1	76	29	12
2	767	729	41
3	240	191	26
4	372	358	10
5	64	21	5
6	382	371	8
7	210	-204	2
8	571	567	3
9	20	-12	0
10	343	370	-17
11	59	4	6
12	177	220	-21
13	115	-47	14
14	239	260	-11
15	-21	-53	-3
16	294	271	12

4 7 L

0	258	-207	28
1	721	662	45
2	130	-120	3
3	583	568	11
4	114	-114	0
5	369	359	6
6	124	-141	-5
7	350	356	-3
8	238	-253	-6
9	420	419	0
10	-96	-11	-17
11	275	304	-19
12	69	34	4
13	270	237	18
14	-89	-57	-12
15	208	222	-5

4 8 L

0	679	620	43
1	41	-22	1
2	569	551	12
3	187	128	21
4	698	656	29
5	169	-186	-6
6	512	530	-12
7	108	-100	1
8	454	434	13
9	39	-44	0
10	254	275	-11
11	-113	-7	-15
12	242	264	-11
13	78	-80	0
14	253	236	8

4 9 L

0	-113	-68	-20
1	530	495	23
2	136	98	9
3	510	521	-7
4	171	145	8
5	669	643	17
6	70	-52	3
7	392	406	-11
8	-31	-85	-10
9	254	269	-8
10	47	-10	2
11	291	306	-8
12	-90	-50	-11
13	232	250	-8

4 10 L

0	449	437	7
1	-98	17	-10
2	389	345	24
3	48	-19	3
4	388	386	1
5	-44	-89	-12
6	370	402	-23
7	-129	-38	-22
8	229	257	-15
9	-74	9	-6
10	212	202	4
11	-65	-51	-7

4 11 L

0	111	-3	15
1	225	220	2
2	40	-73	-4
3	353	346	4
4	137	-35	21
5	359	378	-13
6	96	-18	10
7	226	257	-15
8	-34	-26	-2
9	199	181	7

4 12 L

0	328	336	-4
1	113	-29	13
2	334	331	1
3	-40	-62	-6
4	271	287	-8
5	121	-36	14
6	237	253	-7
7	-161	18	-25

4 13 L

0	92	23	8
1	292	265	14
2	-50	-107	-13
3	253	280	-13

5 0 L

0	1008	1052	-34
2	1074	1185	-83
4	971	983	-8
6	758	775	-19
8	340	339	0
10	438	462	-17
12	489	482	4
14	419	402	12
16	149	176	-9

5 1 L

0	-22	53	-9
1	596	629	-44
2	270	-286	-17
3	965	1025	-65
4	34	-22	1
5	910	916	-6
6	120	-83	19
7	424	452	-23
8	110	6	17
9	532	550	-13
10	168	-138	11
11	540	562	-16
12	-118	-26	-16
13	432	423	6
14	74	-16	6
15	270	221	26
16	-83	-56	-11
17	235	182	22

5 2 L

0	884	968	-99
1	231	-240	-9
2	685	736	-64
3	416	-430	-17
4	720	760	-46
5	-49	80	-19
6	600	637	-31
7	222	236	-7
8	608	652	-36
9	94	-67	5
10	462	441	14
11	141	-100	10
12	369	354	8
13	94	71	5
14	274	264	6
15	-84	46	-11
16	232	202	13

5 3 L

0	91	-107	-7
1	761	824	-76
2	104	-103	0
3	773	754	21
4	-65	-26	-11
5	789	811	-24
6	0	26	0
7	545	568	-18
8	-113	-39	-18
9	377	380	-2
10	163	-163	0
11	386	373	7
12	-52	42	-8
13	195	219	-12
14	71	106	-7
15	238	196	20
16	-15	17	0

5 4 L

0	1192	1225	-31
1	86	-51	10
2	1061	1045	15
3	-28	-50	-7
4	572	548	20
5	-17	-5	0
6	534	540	-4
7	-45	-79	-10
8	733	720	9
9	164	-154	3
10	465	449	10
11	130	-134	-1
12	289	279	6
13	99	15	12
14	188	250	-28
15	-130	-2	-19
16	230	225	2

5 5 L

0	-30	18	-2
1	936	904	38
2	-93	-8	-13
3	737	697	31
4	53	-65	-1
5	540	542	-1
6	37	-18	1
7	619	607	8
8	126	-96	7
9	501	491	6
10	-89	-19	-9
11	317	311	4
12	-115	-62	-21
13	234	246	-6
14	94	-61	6
15	263	261	1

5 6 L

0	941	882	42
1	-76	14	-8
2	749	715	25
3	176	130	18
4	360	355	3
5	110	-113	0
6	483	469	9
7	103	-74	6
8	445	442	2
9	-46	-36	-3
10	246	270	-14
11	-74	29	-8
12	111	147	-11
13	36	-23	1
14	281	245	19

5 7 L

0	271	-207	33
1	766	736	22
2	37	-30	0
3	535	547	-8
4	107	61	9
5	468	447	14
6	53	-106	-9
7	447	434	8
8	37	9	1
9	371	387	-12
10	73	47	4
11	224	247	-12
12	80	-25	7
13	183	194	-4
14	83	-70	2

5 8 L

0	528	503	17
1	-89	12	-9
2	617	573	31
3	-95	-8	-10
4	589	570	13
5	29	-66	-3
6	624	601	15
7	-79	-39	-13
8	402	398	3
9	55	48	0
10	309	290	12
11	74	13	6
12	307	297	5
13	-52	-66	-7

5 9 L

0	53	20	2
1	376	366	6
2	128	93	8
3	502	487	9
4	-16	-31	-2
5	490	477	10
6	128	-144	-5
7	340	347	-5
8	58	-60	0
9	275	266	5
10	86	21	7
11	300	287	7

5 10 L

0	420	417	3
1	87	-39	7
2	381	365	11
3	101	-101	0
4	417	427	-7
5	82	-70	2
6	337	308	19
7	-84	-62	-12
8	195	223	-12
9	-15	-28	-1
10	217	225	-3

5 11 L

0	126	-110	4
1	299	307	-4
2	102	-112	-2
3	358	372	-9
4	89	-86	0
5	350	342	4
6	-48	-11	-2
7	212	229	-7
8	98	-45	8

5 12 L

0	288	272	8
1	-115	-73	-19
2	257	292	-17
3	64	-81	-2
4	248	269	-10
5	-55	-26	-3

6 0 L

0	584	570	12
2	771	828	-46
4	915	989	-81
6	514	534	-16
8	307	313	-3
10	421	398	14
12	391	388	2
14	220	216	2

6 1 L

0	23	95	-20
1	618	656	-45
2	83	-68	5
3	890	904	-15
4	200	-188	6
5	461	491	-24
6	97	-17	12
7	436	463	-20
8	46	-75	-4
9	420	403	11
10	-87	-41	-10
11	434	441	-6
12	-75	21	-7
13	266	268	-1
14	39	-20	1
15	156	182	-9

6 2 L

0	834	889	-63
1	323	-308	15
2	750	751	0
3	187	-213	-24
4	587	622	-30
5	106	124	-6
6	588	593	-3
7	56	79	-4
8	421	436	-10
9	140	-128	3
10	397	364	19
11	32	-71	-7
12	355	339	11
13	90	8	10
14	206	228	-9
15	46	-12	2

6 3 L

0	54	-66	-3
1	1005	974	29
2	236	-238	-2
3	793	790	2
4	49	19	2
5	797	793	3
6	182	217	-16
7	484	493	-6
8	132	-97	9
9	472	448	16
10	131	-73	13
11	292	272	13

12	68	29	5
13	265	241	12
14	-85	36	-10
15	139	177	-12

6 4 L

Ø	909	880	35
1	153	-130	8
2	750	735	11
3	-117	6	-19
4	486	473	9
5	163	89	24
6	602	596	4
7	-19	-61	-5
8	575	564	7
9	106	-116	-2
10	325	330	-4
11	86	-24	9
12	249	221	15
13	78	Ø	7
14	235	215	9

6 5 L

Ø	110	19	16
1	619	609	7
2	76	-71	Ø
3	474	440	25
4	-32	-59	-5
5	432	427	3
6	-133	-34	-23
7	511	485	18
8	126	-76	10
9	405	393	12
10	80	-108	-6
11	243	255	-6
12	134	-63	17
13	265	234	16
14	-22	-50	-3

6 6 L

Ø	865	811	38
1	-45	10	-2
2	476	441	25
3	116	12	17
4	386	383	1
5	133	-87	11
6	500	482	12
7	163	-132	9
8	474	464	11
9	98	32	11
10	310	308	1
11	111	39	13
12	196	209	-5
13	-51	-58	-6

6 7 L

Ø	111	-98	3
1	573	540	24
2	-62	-4	-4
3	490	481	6
4	95	-94	Ø
5	425	406	12
6	75	-57	2
7	476	460	12
8	132	69	16
9	350	349	Ø
10	93	44	8
11	295	245	28
12	15	-9	Ø

6 8 L

Ø	496	485	7
1	75	35	4
2	473	466	4
3	55	-6	3
4	543	518	16
5	138	-163	-11
6	374	353	14
7	123	-63	13
8	266	237	15
9	47	28	1
10	217	225	-3
11	150	-19	24

6 9 L

Ø	76	56	2
1	369	355	13
2	132	65	21
3	378	361	12
4	91	-111	-4
5	402	408	-4
6	109	-128	-5
7	225	230	-2
8	-94	-59	-14
9	238	200	18
10	107	-25	11

6 10 L

Ø	315	281	21
1	-55	-91	-13
2	319	340	-13
3	78	-20	6
4	328	319	5
5	72	-71	Ø
6	276	256	11
7	38	-54	-1
8	247	226	9

6 11 L

Ø	14	-54	-3
1	287	272	8
2	141	-147	-1
3	338	349	-6
4	-65	-77	-10
5	290	282	3
6	-89	-26	-8

6 12 L

Ø	269	258	5
1	82	-75	1
2	304	310	-3

7 Ø L

Ø	559	532	30
2	679	721	-35
4	690	703	-10
6	226	214	5
8	242	265	-11
10	384	381	2
12	317	282	22
14	166	160	2

7 1 L

Ø	61	38	6
1	513	519	-5
2	-99	-28	-16
3	463	476	-9
4	98	140	-13
5	461	486	-18
6	-81	-59	-13
7	274	286	-6
8	76	-5	7
9	348	344	2
10	-43	-14	-2
11	341	311	20
12	-14	39	-2
13	195	169	10
14	-60	-13	-4

7 2 L

Ø	453	481	-23
1	159	-120	15
2	563	574	-9
3	Ø	-8	Ø
4	451	466	-11
5	124	133	-2
6	423	420	2
7	-56	34	-5
8	430	398	19
9	129	-73	12
10	376	350	19
11	-90	-15	-10
12	232	207	11
13	136	51	19
14	206	160	17

7 3 L

Ø	221	-223	-1
1	612	619	-5
2	251	-256	-2
3	586	581	3
4	84	74	1
5	549	538	7
6	102	9	12
7	479	476	2
8	86	-70	2
9	339	320	17
10	73	-33	5
11	274	264	5
12	-84	44	-10
13	255	236	9
14	-78	2	-6

7 4 L

Ø	647	639	6
1	112	-95	4
2	520	490	22
3	-77	5	-7
4	408	375	22
5	-43	-44	-4
6	525	493	21
7	140	-103	9
8	372	381	-8
9	108	-74	8
10	257	220	20
11	71	-22	5
12	165	162	1
13	-22	Ø	Ø

7 5 L

Ø	128	66	15
1	445	443	1
2	42	-39	Ø
3	363	338	15
4	-86	-33	-9
5	341	346	-3
6	85	-29	7
7	417	389	28
8	99	-122	-6
9	208	221	-6
10	-67	-27	-6
11	227	188	17
12	-65	-10	-4

7 6 L

Ø	632	615	12
1	75	-43	4
2	372	367	3
3	-63	-50	-8
4	381	345	21
5	192	-154	12
6	377	350	26
7	59	-63	Ø
8	367	365	1
9	134	54	18
10	252	229	11
11	78	-13	6
12	229	221	3

7 7 L

Ø	172	-149	7
1	465	455	6
2	109	-55	10
3	351	344	3
4	28	-79	-9
5	421	390	23
6	110	-43	13
7	338	322	10
8	39	14	1
9	278	238	21
10	81	-39	5
11	205	193	4

7 8 L

Ø	368	331	21
1	-73	27	-6
2	460	442	18
3	-93	-69	-16
4	377	351	19
5	126	-134	-2
6	317	275	26
7	51	-24	2
8	113	174	-17
9	100	3	11
10	161	141	5

7 9 L

Ø	44	36	Ø
1	279	257	12
2	73	-74	Ø
3	353	346	4
4	118	-121	Ø
5	252	274	-11
6	96	-114	-4
7	190	189	Ø
8	-133	-38	-20

7 10 L

Ø	238	248	-5
1	68	4	5
2	304	276	15
3	153	-53	24
4	277	229	25
5	105	-45	10
6	106	178	-19

7 11 L

Ø	-55	-50	-6
1	271	246	12
2	31	-61	-2
3	272	285	-7

8 Ø L

Ø	407	411	-3
2	616	615	Ø
4	353	383	-19
6	253	219	16
8	270	281	-7
10	284	275	5
12	252	220	15

8 1 L

Ø	190	-175	6
1	443	456	-9
2	26	80	-7
3	574	561	9
4	51	-11	3
5	317	309	4
6	104	31	11
7	284	253	15
8	91	9	11
9	305	295	6
10	98	56	8
11	253	236	8
12	146	48	21
13	175	132	13

8 2 L

Ø	583	600	-13
1	106	-65	8
2	489	493	-3
3	-94	44	-13
4	301	292	5
5	176	150	9
6	289	288	Ø
7	68	-53	3
8	306	309	-1
9	-108	-44	-17
10	259	232	14
11	106	31	12
12	205	156	18

8 3 L

Ø	221	-203	8
1	421	412	6
2	-50	-8	-3
3	372	367	3
4	63	51	1
5	384	350	20
6	83	5	7
7	249	264	-11
8	-49	-86	-12
9	258	211	25
10	75	-29	5
11	216	191	10

12	-38	8	-1

8 4 L

Ø	446	45Ø	-3
1	-9Ø	-71	-16
2	363	341	13
3	74	23	5
4	372	354	1Ø
5	91	-17	8
6	4Ø1	375	25
7	97	-51	9
8	298	288	6
9	138	-96	11
1Ø	158	132	8
11	43	1Ø	1
12	198	136	21

8 5 L

Ø	83	89	-1
1	258	272	-7
2	88	1Ø	9
3	249	216	15
4	-21	-2	Ø
5	4Ø6	376	28
6	-1Ø2	-71	-19
7	267	274	-4
8	41	-71	-3
9	15Ø	18Ø	-1Ø
1Ø	-75	-28	-7
11	2Ø2	174	1Ø

8 6 L

Ø	3Ø1	295	2
1	-58	1	-3
2	134	156	-6
3	71	-56	3
4	268	233	21
5	121	-111	2
6	326	3Ø9	1Ø
7	36	-16	1
8	234	227	3
9	-1Ø7	-2	-12
1Ø	193	169	8

8 7 L

Ø	137	-72	14
1	269	259	7
2	46	-75	-4
3	314	289	16
4	11Ø	-112	Ø
5	284	295	-6
6	53	-41	1
7	228	237	-4
8	-94	17	-1Ø
9	2Ø6	167	14

8 8 L

Ø	374	4Ø2	-2Ø
1	-55	-36	-5
2	378	378	Ø
3	84	-141	-14
4	275	3Ø2	-15
5	137	-94	11
6	214	213	Ø
7	8Ø	-22	6
8	143	131	3

8 9 L

Ø	77	-12	6
1	317	3Ø2	9
2	92	-47	7
3	318	3Ø9	5
4	154	-135	5
5	245	227	8
6	1Ø4	-89	3

8 1Ø L

Ø	223	218	2
1	155	-46	24
2	264	251	6
3	95	-31	8
4	2Ø1	196	2

8 11 L

Ø	-112	-58	-15

9 Ø L

Ø	443	454	-8
2	397	368	18
4	325	32Ø	2
6	198	188	5
8	228	235	-3
1Ø	3Ø7	252	29

9 1 L

Ø	11Ø	-125	-4
1	5Ø5	539	-24
2	63	5	4
3	389	38Ø	5
4	-55	4Ø	-5
5	3Ø4	294	8
6	77	-18	7
7	254	26Ø	-3
8	-38	-2Ø	-2
9	293	25Ø	22
1Ø	8Ø	45	5
11	171	17Ø	Ø

9 2 L

Ø	441	44Ø	Ø
1	168	-191	-9
2	459	436	14
3	114	75	8
4	328	311	9
5	43	-17	2
6	299	293	3
7	112	-87	6
8	227	241	-6
9	7Ø	-21	5
1Ø	2Ø2	186	6
11	-31	13	-1

9 3 L

Ø	97	-12Ø	-5
1	282	295	-7
2	116	-9Ø	5
3	326	314	6
4	78	39	8
5	241	246	-3
6	-37	-21	-2
7	242	216	12
8	59	-41	2
9	176	153	8
1Ø	79	3	6

9 4 L

Ø	365	375	-6
1	99	-48	8
2	335	319	9
3	58	-13	5
4	311	288	15
5	-148	-22	-27
6	282	3Ø5	-13
7	125	-71	12
8	162	167	-1
9	-26	Ø	Ø
1Ø	1Ø2	1Ø3	Ø

9 5 L

Ø	134	-19	18
1	298	258	2Ø
2	77	-72	1
3	247	274	-15
4	-81	-66	-13
5	32Ø	3Ø6	8
6	125	-78	11
7	241	22Ø	1Ø
8	1Ø2	-49	9
9	178	154	8

9 6 L

Ø	265	286	-12
1	57	8	4
2	115	163	-15
3	111	-43	13
4	228	215	6
5	89	-24	8
6	256	191	3Ø
7	-88	-16	-8
8	193	165	9

9 7 L

Ø	-85	71	-15
1	194	225	-14
2	32	21	Ø
3	198	21Ø	-5
4	42	-42	Ø
5	188	2Ø5	-6
6	-41	36	-3
7	188	153	12

9 8 L

Ø	279	284	-3
1	61	-33	3
2	3ØØ	294	3
3	-61	-55	-7
4	287	265	11
5	1ØØ	-57	7

9 9 L

Ø	-4Ø	-6	-1
1	289	27Ø	9
2	121	-92	6
3	273	268	2

9 1Ø L

Ø	251	199	23

1Ø Ø L

Ø	265	255	5
2	363	354	7
4	198	178	8
6	18Ø	182	Ø
8	236	229	3

1Ø 1 L

Ø	182	-164	6
1	3Ø3	32Ø	-8
2	-51	-16	-4
3	232	243	-5
4	87	1	9
5	185	216	-14
6	-66	-37	-6
7	2Ø8	2Ø5	1
8	-1Ø5	-19	-12
9	198	19Ø	3

1Ø 2 L

Ø	418	414	2
1	93	2	14
2	346	33Ø	11
3	-1Ø4	15	-14
4	279	245	19
5	1Ø3	-46	1Ø
6	219	197	9
7	11Ø	-62	9
8	274	226	23
9	74	-27	5

1Ø 3 L

Ø	-1Ø2	-27	-18
1	346	334	9
2	123	48	16
3	332	317	1Ø
4	95	8	11
5	282	252	16
6	135	-65	15
7	245	199	2Ø
8	163	-31	28

1Ø 4 L

Ø	364	355	7
1	24	7	Ø
2	279	275	2
3	1Ø7	-9	14
4	289	3Ø3	-8
5	-51	-7Ø	-8
6	238	221	8
7	133	-45	16
8	166	129	1Ø

1Ø 5 L

Ø	-77	-9	-7
1	199	223	-11
2	-43	-25	-3
3	279	26Ø	1Ø
4	11Ø	-69	8
5	326	294	18
6	76	-59	2
7	222	185	14

1Ø 6 L

Ø	286	286	Ø
1	-126	-45	-2Ø
2	291	28Ø	6
3	9Ø	-23	8
4	281	255	13
5	1Ø7	-41	1Ø
6	2Ø5	222	-6

1Ø 7 L

Ø	78	-32	5
1	279	265	7
2	119	-88	7
3	181	221	-14
4	99	-26	9

1Ø 8 L

Ø	16Ø	197	-13
1	95	-52	6
2	2Ø1	216	-6

11 Ø L

Ø	327	3Ø8	12
2	185	198	-5
4	135	121	4
6	177	182	-1

11 1 L

Ø	88	-16	9
1	314	3Ø5	5
2	35	56	-2
3	22Ø	21Ø	4
4	116	13	15
5	167	156	3
6	35	-27	Ø

11 2 L

Ø	383	384	Ø
1	71	17	5
2	314	312	1
3	12Ø	75	9
4	2Ø7	199	3
5	-122	18	-15
6	21Ø	178	11

11 3 L

Ø	Ø	7	Ø
1	23Ø	255	-12
2	-29	47	-3
3	271	249	11
4	5Ø	-1	2
5	275	225	24
6	92	-19	8

11 4 L

Ø	214	189	11
1	-83	Ø	-7
2	262	218	22
3	-71	-37	-7
4	248	221	12
5	-5Ø	-44	-4

11 5 L

Ø	139	-4	23
1	2Ø8	142	24

2	-104	-21	-12
3	242	206	15
4	140	-21	20

11 6 L

0	152	191	-13
1	-49	-19	-2
2	152	191	-12

3	55	-35	1

11 7 L

0	44	-50	0
1	162	194	-10

12 0 L

0	235	212	10
2	209	178	11

12 1 L

0	76	46	4
1	269	211	28
2	15	49	-2
3	104	145	-9

12 2 L

0	257	231	12
1	34	-34	0
2	209	181	10
3	22	0	0

12 3 L

0	-84	-34	-8
1	220	175	17
2	92	-36	7

12 4 L

0	114	154	-10
1	-106	4	-11

12 5 L

0	-57	-35	-4

Appendix D. Publications.

Reprinted from the Journal of the American Chemical Society, 1982, *104*, 7352.

Substrate Organometallic Chemistry of Osmium Tetraoxide: Formation of a Novel Type of Carbon Dioxide Coordination

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Contribution No. 6695 from the Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, California 91125

Received August 12, 1982

As part of our general interest in the chemistry available to oxidizing compounds we have begun to investigate the principal interactions available to osmium tetraoxide and related molecules with classical organometallic entities such as Vaska's complex, *trans*-$IrCl(CO)(PPh_3)_2$. In this communication we report on the result of the oxidative-addition reaction of osmium tetraoxide to Vaska's complex in the presence of pyridine bases, a reaction that yields a dinuclear carbon dioxide adduct. This result provides a first glimpse at the substrate organometallic chemistry of osmium tetraoxide. A new type of carbon dioxide coordination has been discovered here.[2]

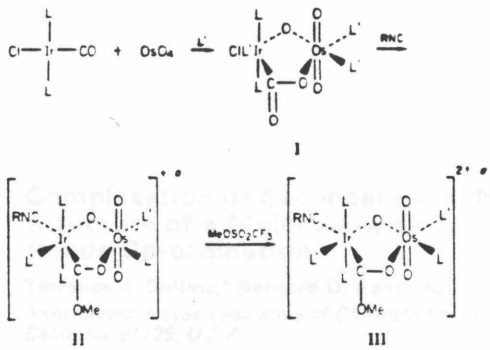
When 1 equiv of Vaska's complex is added to osmium tetraoxide in toluene at −78 °C and the mixture is allowed to warm to room temperature, a gradual color change from yellow to orange-brown occurs. A brown powder can be isolated by precipitation with hexanes, and orange-brown crystals of the air stable compound I (see Scheme I) form upon recrystallization from dichloromethane–*tert*-butylpyridine–di-*n*-butyl ether. Compound I reacts readily at room temperature with *tert*-butyl isocyanide in dichloromethane to give the air-stable olive-green dinuclear salt, II, in high yield. We assume the coordination environment at iridium in II is as depicted in the scheme since treatment of II

(1) Myron A. Bantrell Research Fellow, 1981–1983, the California Institute of Technology.

(2) Structurally characterized carbon dioxide complexes include $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ (Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636. Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708). $[Co(pr\text{-}salen)K(\mu\text{-}CO_2)(THF)]_n$ (Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *101*, 74). $[(Ph_3P)_2N][HOs_3(CO)_{10}O_2CO_{Os_4}(CO)_{13}]$ (Guy, J. J.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1978**, B34, 1718), and $Nb(\eta^5\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)$ (Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

0002-7863/82/1504-7352$01.25/0

Scheme I



L = triphenylphosphine
L' = 4-*tert*-butylpyridine
R = *tert*-butyl

[a] Isolated and characterized as the perchlorate salt.

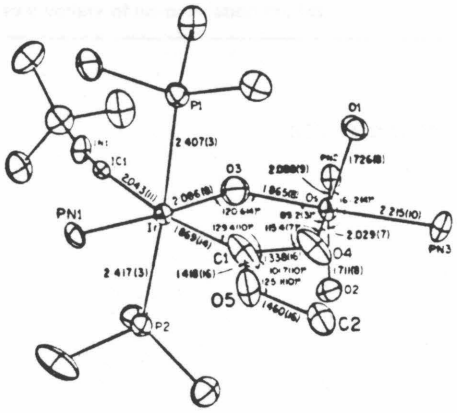


Figure 1. Molecular structure of the dication $[(PPh_3)_2(t\text{-BuNC})(4\text{-}t\text{-Bupy})Ir(\mu\text{-O})(\mu\text{-C[OMe]O})Os(O)_2(4\text{-}t\text{-Bupy})_2]^{2+}$.

with methyl trifluoromethanesulfonate in dry benzene yields a brown precipitate which, after perchlorate exchange, affords brown crystals of the air-stable carbene-containing compound III.[3] An X-ray crystal structure analysis of III is consistent with methylation proceeding at the exocyclic oxygen atom of the bridging carbon dioxide moiety (see Figure 1).[4] The *O*-methyl and nonmethylated oxygen atoms of the carbene ligand are cis, and NMR evidence (−70 to 40 °C) suggests either the presence of only one of the two possible carbene isomers in solution or free rotation about the C1–O5 bond occurring in solution.

Table I. ^{31}P and ^{13}C NMR Data[a] (δ)

compd	^{31}P,[b] δ	^{13}C,[c] δ	$^2J_{^{13}C-^{31}P}$, Hz[d]
I	−14.0	187.2	7.0
II	−18.2	207.5	8.8
III	−19.2	221.1	8.8

[a] JEOL FX 90Q, solvent $CDCl_3$. [b] Relative to external standard H_3PO_4. [c] Relative to internal standard Me_4Si. [d] Obtained from ^{13}C and ^{31}P spectra.

Table II. Relevant Infrared Data (cm^{-1})

compd	νC=O	νC–O	ν_{OsO_2}	νN≡C
I	1593	1022	820	
I-^{13}C	1560	1010	820	
I-^{18}O	1592	1010	780	
II	1583	*a*	823	2180
II-^{13}C	1555	*a*	823	2180
II-^{18}O	1583	*a*	785	2180

compd	CO_2Me	ν_{OsO_2}	νN≡C
III	1255	840	2200
III-^{13}O	1230	840	2200
III-^{18}O	1255	800	2200

[a] Obscured by ClO_4^- bands.

The formulation of compounds I and II as dinuclear bridging carbon dioxide complexes follows from the X-ray analysis of III and is additionally supported by the appropriate ^1H, ^{31}P, and ^{13}C NMR spectra and by IR experiments with ^{13}C- and ^{18}O-labeled materials (see Tables I and II). Label enrichment was based on the use of *trans*-$IrCl(^{13}CO)(PPh_3)_2$ (99% enriched) and $Os^{18}O_4$ (88% enriched), and the IR bands corresponding to the bridging CO_2 ligand have been identified by the isotopically induced band shifts. The ν(C=O) band for I at 1593 cm^{-1} shifts to 1560 cm^{-1} upon ^{13}C substitution. A similar shift is observed for II. A band at 1022 cm^{-1} in I shifts to 1010 upon ^{13}C or ^{18}O substitution, confirming that the bridging carbon dioxide ligand is constructed from the iridium carbonyl ligand and the oxo ligand from osmium tetraoxide. The coordination at the osmium center is also well characterized from the IR spectral data. The very strong trans-$Os^{16}O_2$ asymmetric stretching band can be identified at 820, 823, and 840 cm^{-1} for compounds I–III, respectively. These bands fall in the expected region[5] and have been confirmed by isotopic substitution.

The ^{13}C and ^{31}P NMR spectra provide evidence for the presence of equivalent phosphine ligands in each compound. The ^{13}C-enriched carbon dioxide signal in I is a triplet at δ 187.2 ($^2J_{^{13}C-^{31}P}$ = 7.0 Hz), which shifts to δ 207.2 in II and δ 221 in III.[6] The ^1H NMR spectra of compounds I and II exhibit considerable temperature dependence. Our evidence suggests this feature is due to lability of the *tert*-butylpyridine ligands on osmium(VI) but not to lability at the iridium center. We will describe this chemical property more fully at a later date.

The X-ray crystal structure of III shows the expected existence of multiple bonding between the carbene carbon atom and the oxygen hetero atoms. It is interesting to note that the C1–O4 bond length [1.338 (16) Å] is significantly shorter than the C1–O5 bond length [1.418 (16) Å] suggesting that the CO_2Me unit might also be described as a bridging ester ligand.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., the Atlantic Richfield Corp. of America, and Occidental Research Inc. for support of this research.

Supplementary Material Available: Listings of fractional atomic coordinates, Gaussian amplitudes, bond distances and angles, and structure factor amplitudes (62 pages). Ordering information is given on any current masthead page.

(3) Elemental analysis data: all solvates quantified by NMR. Calcd for I-$^1/_3Bu_2O$: C, 53.97; H, 5.10; N, 2.83. Found: C, 54.15; H, 5.29; N, 2.80. Calcd for II-H_2O: C, 51.63; H, 5.02; N, 3.49. Found: C, 51.49; H, 4.95; N, 3.53. Calcd for III-1.25H_2O (0.25 CH_2Cl_2): C, 48.34; H, 4.85; N, 3.21. Found: C, 48.33; H, 4.81; N, 3.21.

(4) Crystal data: space group $P\bar{1}$, a = 21.20 (2) Å, b = 12.800 (5) Å, c = 14.470 (16) Å, α = 85.78 (9)°, β = 94.04 (9)°, γ = 94.41 (9)°, V = 3896 Å^3, Z = 2. Data were collected on a locally modified Syntex P2$_1$ diffractometer with graphite monochromator and Mo Kα radiation (λ 0.710 69 Å) to 2θ = 48° ($+h,\pm k,\pm l$). The averaged data (10 222) were corrected for Lorentz and polarization effects. The Os and Ir atom positions were derived from the Patterson map, and subsequent Fourier maps revealed the remaining non-hydrogen atoms. Least-squares refinement of atomic coordinates and B's, minimizing $\sum w[F_o^2 - (F_c/k)^2]^2$ with weights $w = [\sigma^2(F^2) + (0.02 \times \text{scan counts})^2]^{-1}$ gave $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.13$ (9268 reflections with $F_o^2 > 0$). Introduction of hydrogen atoms from difference maps with B = 5 Å^2 and refinement of all nonhydrogen atoms with anisotropic Gaussian amplitudes resulted in R_F = 0.086 and GOF = 1.66 (R_f = 0.055 for the 6347 reflections with $F_o^2 > 3\sigma(F^2)$).

(5) Schröder, M. *Chem. Rev.* **1980**, *80*, 187.

(6) The ^{13}C NMR signal for the CO_2 ligand in $Nb(\eta^5\text{-}C_5H_4Me)(CH_3SiMe_3)(\eta^2\text{-}CO_2)$ occurs at δ 200.5.[2]

Complexation of Secondary Amides to Chromium(III): the *X*-Ray Structure of a Molecule with Two Modes of Monodentate Organic Amide Co-ordination

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The *X*-ray crystal structure of the dimer $[Cr(H(chba\text{-}Et)\}(py)_2]_2 \cdot 2py$ [H_4(chba-Et) = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane, py = pyridine] establishes, for the first time, the existence of N-co-ordination of an organic amide to Cr^{III}, the N-atom and carbonyl O-atom of two separate amide groups being co-ordinated to each Cr^{III} centre [Cr–N 2.030(6) and Cr–O 1.976(5) Å]; the potentially tetra-anionic chelating ligand leads to a variety of co-ordination modes.

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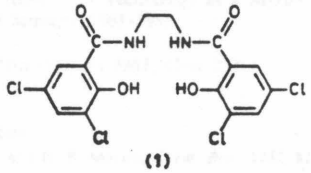
The co-ordination chemistry of organic amides is an important part of a number of current chemical problems.[1–6] Of considerable interest is the lowering of reduction potentials of metal couples, *i.e.*, stabilization of high oxidation states, that accompanies N-co-ordination of the organic amide ligand.[1–4] Our interest in the stabilization of high-valent transition metal complexes has led to an exploration of the co-ordination chemistry of a new ligand, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane [H_4(chba-Et)] (**1**) (Figure 1), with a number of metals. The ligand (**1**) has been designed to be reasonably resistant to oxidation, to form five- and six-membered chelate rings upon co-ordination, to be easily synthesized and derivatized, and to contain the organic amide ligating functional group. It is well recognized that co-ordination of the organic amide group can occur through the nitrogen atom, the oxygen atom, or both.[1,5–7] We report here the crystal structure of an unusual chromium(III) dimer in which both possible types of co-ordination are found. This is the first structural example of the nitrogen atom from an organic amide being co-ordinated to a Cr^{III} metal centre.[8]

Chromium trichloride hexahydrate (0.3 g) was added to pyridine (50 ml) and the mixture was heated under reflux until dissolution was complete. 1 equiv. of (**1**) was added to the boiling chromium–py (py = pyridine) solution, and after 2 min anhydrous sodium carbonate (5 g) was introduced. The mixture was stirred for 2 min and then filtered. Green crystals and a large amount of an amorphous green solid formed on leaving the filtrate in a sealed bottle for several weeks.† A roughly cubic crystal, edge length *ca.* 0.25 mm, was chosen for the *X*-ray study; oscillation photographs showed a small twin component, but other crystals of suitable size were grossly twinned.

Crystal data: $C_{66}H_{48}Cl_8Cr_2N_{16}O_8$, M = 1448.75, monoclinic, space group $P2_1/c$, a = 14.343(4), b = 14.225(3), c = 16.447(8) Å, β = 104.28(3)°, U = 3252(2) Å^3, Z = 2, D_c = 1.48 g cm^{-3}, μ = 7.4 cm^{-1}; data ($+h,\pm k,\pm l$) were collected on a locally modified Syntex $P2_1$ diffractometer with Mo-K_α radiation (λ = 0.71069 Å) up to 2θ = 45°; a total of 8370 intensity measurements were made with θ–2θ scans. The three standard reflections, remeasured after each block of 97 reflections, indicated a 5% linear decay over the exposure time of 206 h. The data were corrected for decomposition, but not for absorption; averaging gave 4279 reflections, 3685 with $I > 0$ and 2031 with $I > 3\sigma(I)$.



(**1**)

Figure 1. The ligand H_4(chba-Et), (**1**).

† Important i.r. spectral data (Nujol, cm^{-1}): 3210 [br., w, ν(N–H)], 1605 (s, sh), 1595 (s, sh), 1580 (sh), 1572 (w, sh), 1550 (br., m), and 1505 (br., s) (spectra identical for both crystalline and amorphous material).

The positions of the chromium atoms were derived from a Patterson map, and the subsequent Fourier and difference Fourier maps indicated the locations of the remaining non-hydrogen atoms; the hydrogen atoms were placed in calculated positions and were not refined. The final cycle of refinement gave a goodness-of-fit of 1.38 and R = 0.122 (R_w = 0.055).‡

The structure consists of discrete dimers and disordered solvent molecules of pyridine. Figure 2 gives bond distances about the Cr centres, which are related by a centre of symmetry. The distorted octahedral environment includes the pyridine nitrogen atoms, an amide nitrogen atom, the phenolic oxygen atoms, and an amide-carbonyl oxygen atom; the co-ordinated pyridine ligands are *cis* and the phenolic oxygen atoms are *trans*.

The carbonyl C–O bond lengths are equal for both co-ordinated and unco-ordinated amide carbonyls 1.278(9) *vs.* 1.270(9) Å. The Cr–N_{amide} bond length is 2.030(6) Å, and the two Cr–O_{phenol} bond lengths are 1.915(5) and 1.931(5) Å, *cf.*, $[Cr\{N,N'$-ethylenebis(salicylideneaminato)$\}(H_2O)_2]Cl$: Cr–N 2.005(9) and 1.997(8) Å, Cr–O 1.916(8) and 1.952(8) Å.[9] The Cr–$O_{carbonyl}$ bond length is 1.976(5) Å, *cf.*, 1.91(2) Å found in *mer*-trichloro-(*N,N*-dimethylformamide)(1,10-phenanthroline)chromium(III).[10] The Cr–N_{py} bond lengths [2.145(6) Å, *trans*-to-N and 2.097(6) Å, *trans*-to-O] indicate a greater *trans*-influence of the N-co-ordinated *vs.* the O-co-ordinated amido ligand. The Cr–Cr distance in the dimer is 8.9 Å.

‡ The CRYM computing system was used (D. J. Duchamp, California Institute of Technology). Least-squares refinement minimized $\Sigma w\Delta^2$ with weights $w = \{[\sigma(F^2)]^2 + (0.02 \times \text{scan counts})^2\}^{-1}$ and $\Delta = F_o^2 - (F_c/k)^2$. The goodness-of-fit is $[\Sigma w\Delta^2/(n-p)]^{1/2}$, $R = \Sigma||F_o| - |(F_c/k)||/\Sigma F_o$ (for reflections with $I>0$) and $R_w = R$ [for reflections with $I > 3\sigma(I)$]. The atomic co-ordinates from this work are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure factor table is available as Supplementary Publication No. SUP 23676 (26 pp.) from the British Library Lending Division. For details of how to obtain this material, see Instructions to Authors, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3.

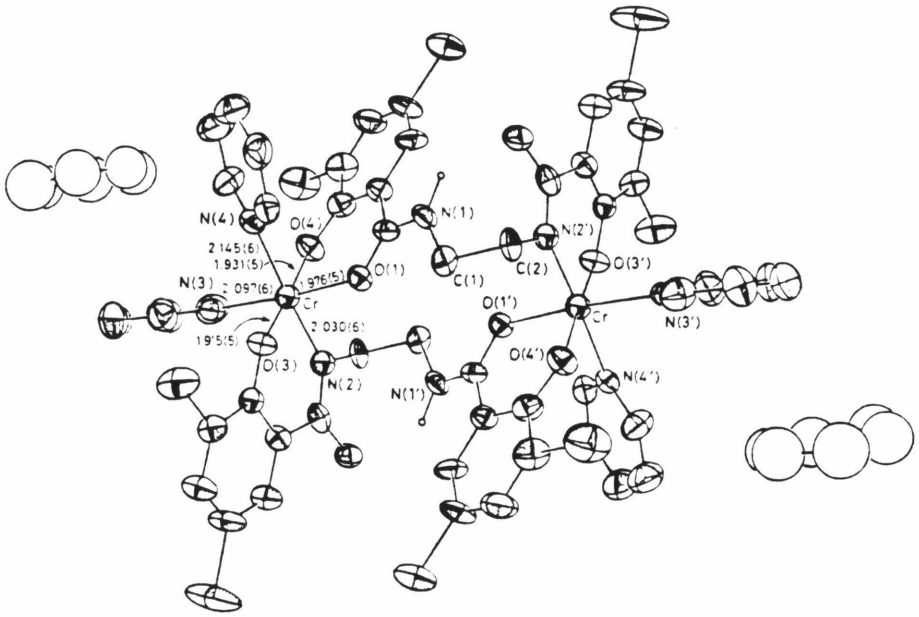


Figure 2. Molecular structure of $[Cr\{H(chba\text{-}Et)\}(py)_2]_2 \cdot 2py$.

The ambidentate behaviour of the organic amide functional group is evident, showing that two types of monodentate co-ordination to Cr^{III} are possible, at least where the amide is part of a chelating system. In structural investigations with metals other than Cr, (**1**) has been found to co-ordinate through the two phenolic oxygen atoms and the two amide nitrogen atoms (all to one metal centre). The strong i.r. band at 1505 cm^{-1} found for the title dimer is not observed in the i.r. spectra of these latter complexes, which exhibit no i.r. bands in the 1500–1520 cm^{-1} region.

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Complexation of a Tetradentate Tetra-anionic Ligand to Osmium(IV): a Step Towards the Development of Multianionic Chelating Ligands for Use in Stabilizing Oxidizing Inorganic Complexes

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The compound 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane [H_4(chba-Et)] (**1**) readily co-ordinates to osmium(VI) as a tetradentate tetra-anion; the *X*-ray crystal structure of the reduced complex, $K_2[\{Os(\eta^4\text{-chba-Et})(OPPh_3)\}_2\text{-}O]$ (**3**), demonstrates that this ligand can bind as a tetradentate tetra-anion to the equatorial sites of a single octahedral metal centre and the potassium ion is found in two unusual co-ordination environments in complex (**3**).

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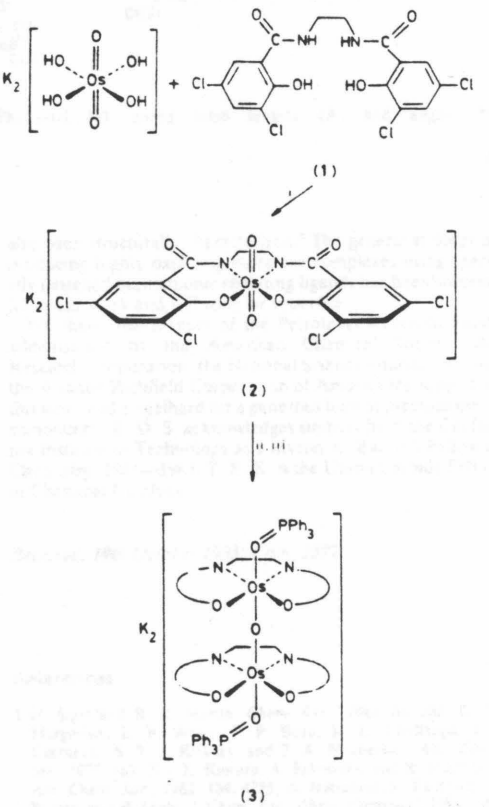
The variety of useful inorganic oxidizing agents presently available is limited by the lack of suitable ligands which can form stable highly oxidizing metal complexes. We are interested in exploring new reactivity in oxidation chemistry and our approach has been to design multianionic chelating ligands to generate new highly oxidizing inorganic complexes. The co-ordination chemistry of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane [H_4(chba-Et)], (**1**) (see Scheme 1), has been investigated as a test case in our work. The ligand (**1**) has been designed to be reasonably resistant to oxidation, to form five- and six-membered chelate rings upon co-ordination, to be easily synthesized and derivatized, and to contain the organic amide functional group which is known to stabilize high oxidation states when *N*-co-ordinated.[1]

We have recently shown[2] that it is possible to co-ordinate (**1**) as a bridging ligand between two chromium(III) centres in which both types of monodentate organic amide co-ordination were found. In this paper we report that it is also possible to co-ordinate (**1**) as a tetradentate tetra-anion to a single metal centre, an important preliminary objective.

Treatment of a colourless acetone solution of (**1**) with a blue solution of $K_2[OsO_2(OH)_4]$ dissolved in methanol results in a colour change to orange. Removal of solvents *in vacuo* followed by recrystallization of the residue from ethanol–diethyl ether affords a quantitative yield of the orange microcrystalline salt $K_2[OsO_2(\eta^4\text{-chba-Et})]$ (**2**).† This octahedral *trans*-dioxo osmium(VI) complex is diamagnetic as expected.[3] Reduction of this compound with triphenylphosphine (2.5 mol per mol of osmium) in tetrahydrofuran followed by addition of CH_2Cl_2 resulted on one occasion in the deposition of dark crystals of the μ-oxo bridged osmium(IV) dinuclear species, $K_2[\{Os(\eta^4\text{-chba-Et})(OPPh_3)\}_2\text{-}O]$ (**3**), which has been characterized by an *X*-ray crystal structure determination.

Crystal data for (**3**): $C_{68}H_{46}Cl_8K_2N_4O_{12}Os_2P_2\cdot 3\frac{1}{2}C_3H_6O\cdot H_2O$, M = 2004.45, monoclinic, space group $P2_1/c$, a = 18.72(1), b = 15.290(9), c = 28.24(2) Å, β = 107.49(5)°, U = 7709(9) Å^3, Z = 4, D_c = 1.727(2) g cm^{-3}, μ = 3.98 mm^{-1}; data ($+h$, $+k$, $\pm l$) were collected on a locally modified Syntex $P2_1$ diffractometer with Mo-K_α radiation (λ = 0.7107 Å) up to 2θ = 36°; a total of 6065 intensity measurements were made with 6° min^{-1} θ–2θ scans. The three standard reflections, remeasured after each block of 97 reflections, indicated a 16% linear decay. The data were corrected for decomposition, but not for absorption; averaging gave 5331 reflections, 4900 with $I > 0$ and 3411 with $I > 3\sigma(I)$.



Scheme 1. i, Acetone–MeOH; ii, Ph_3P, heat; iii, acetone–tetrahydrofuran–O_2.

The positions of the osmium atoms were derived from a Patterson map, and the subsequent Fourier and difference Fourier maps indicated the locations of the remaining non-hydrogen atoms; the hydrogen atoms were placed at calculated positions and were not refined. The Gaussian amplitudes of the μ-oxo and H-atom co-ordinates (U = 0.035 and 0.063 Å^2) and the population of the unco-ordinated acetone molecule (set to 0.5) were not refined either. The final cycle of refinement gave a goodness-of-fit of 2.03 and

† Satisfactory elemental analyses were obtained. I.r. (ν, cm^{-1}) 820s ($Os^{16}O_2$), 788s ($Os^{18}O_2$). ^{1}H N.m.r. (CD_3COCD_3) δ 8.21 [d, 2 H, ^4J(H–H) 3 Hz] and 7.27 [d, 2 H, ^4J(H–H) 3 Hz] (aromatic C–H), 3.88 (s, 4 H) (N–CH_2CH_2–N).

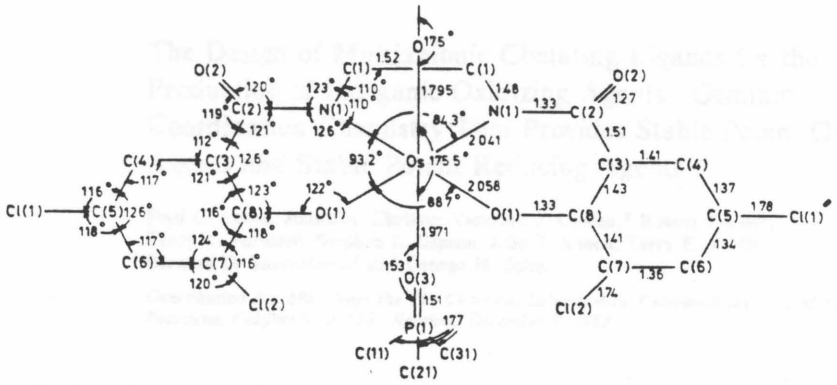


Figure 1. Schematic representation of $K_2[\{Os(\eta^4\text{-chba-Et})(OPPh_3)\}_2\text{-}O]$ (**3**), giving bond lengths (Å) and angles (°). O(3)–P(1)–C(av.) 110°, C–P(1)–C(av.) 108°.

$R = 0.111$ ($R_{3\sigma} = 0.076$);‡ the number of parameters was 503. Figure 1 gives the average (over the four sets of chemically equivalent) bond lengths and angles for the dianion of the molecule.

This structure exhibits the first examples of bonds between Os^{IV} and an *N*-co-ordinated organic amido ligand, a phenoxide ligand, and a phosphine oxide ligand; related structural studies have been performed.[4] This study also reveals unusual co-ordination environments for the potassium ions. One potassium ion, centred in a square pyramid, is well within bonding distance for the four phenolic oxygen atoms [K^+–O(phenol) av. = 2.87 Å] and one acetone solvate molecule [K^+–O(acetone) = 2.80 Å]; this potassium ion is further co-ordinated to the μ-oxo ligand [K^+–O(oxo) = 3.16 Å]. The second potassium ion is apparently four co-ordinate, situated at the centre of a distorted tetrahedron, linking adjacent anions by bonding with two pairs of eclipsed organic amido oxygen atoms, one pair from each dinuclear unit [K^+–O(amide) av. = 2.66 Å]. Low co-ordination numbers for potassium ions are rare.[5] The close interligand contacts of the bis-hydroxybenzamido ligands in this eclipsed conformation are predominantly Cl···Cl contacts, ranging from 3.6 to 3.9 Å, close to the sum of van der Waals' radii for Cl (*ca.* 3.6 Å). Presumably the co-ordination of the potassium ions plays a significant role, and results in the observed eclipsed conformation of the two planar ligands. The dinuclear octahedral Os^{IV} oxo-bridged structure has been observed previously in the complex $Cs_4[\{OsCl_5\}_2\text{-}\mu\text{-}O]$[6] and a bent oxo-bridged dinuclear Os^{IV} complex, $Os_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2Cl_4(PPh_3)_2$, has also been structurally characterized.[7] The general strategy of producing highly oxidizing inorganic complexes using specially designed multianionic chelating ligands has been successful in our work and will soon be reported.

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, the National Science Foundation, and the Atlantic Richfield Corporation of America for support of this work and Engelhard for a generous loan of precious metal compounds. B. D. S. acknowledges support from the California Institute of Technology as a Myron A. Bantrell Fellow in Chemistry, 1981—1983. T. E. K. is the Union Carbide Fellow in Chemical Catalysis.

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‡ The CRYM computing system was used (D. J. Duchamp, California Institute of Technology). Least-squares refinement minimizes $\Sigma\omega\Delta^2$ with weights $\omega^{-1} = \{[\sigma(I)]^2 + (0.02 \times \text{scan counts})^2\}$ (k^2/Lp)^2 and $\Delta = F_O^2 - (F_c/k)^2$. The goodness-of-fit is $\sqrt{[\Sigma\omega\Delta^2/(n-p)]}$. $R = \Sigma||F_O| - |(F_c/k)||/\Sigma F_O$ (for reflections with $I > 0$). $R_{3\sigma} = R$ [for reflections with $I > 3\sigma(I)$]. The atomic co-ordinates from this work are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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The Design of Multianionic Chelating Ligands for the Production of Inorganic Oxidizing Agents. Osmium Coordination Chemistry That Provides Stable Potent Oxidizing Agents and Stable Potent Reducing Agents

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Abstract: The design of multianionic chelating ligands for use in producing new oxidizing agents is discussed. Two potentially tetradentate tetraanionic ligands, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane (H_4CHBA-Et (**1**)) and 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene (H_4CHBA-DCB (**2**)) were synthesized and found to coordinate to osmium as tetradentate tetraanions. X-ray crystal structures of two osmium(IV) complexes of this ligand class are reported: octahedral Os(η^4-CHBA-Et)(py)$_2$ (**5**) has axial pyridine ligands with the tetradentate tetraanion coordinated to the equatorial positions, whereas in Os(η^4-CHBA-DCB)(bpy) (**15**) the bpy ligand occupies one axial and one equatorial position with one phenolic donor in an axial position and the remaining donors of the tetradentate tetraanion coordinated equatorially. Ligand **1** forms osmium complexes in oxidation states II, III, IV, and VI. Attempted electrooxidation of the osmium(IV) complex, **5**, to an osmium(V) complex results in oxidation of the tetradentate tetraanion at the ethylene unit bridging the amide nitrogen atoms. In the presence of alcohol or water this oxidation proceeds in a stepwise manner and several key intermediates have been isolated, independently synthesized, and characterized. The first intermediate isolated results from dehydrogenation of the ligand bridge. In the second intermediate, the unsaturated bridge has been oxidized to a 1,2 diether. Finally, cleavage of the carbon–carbon bond and dealkylation of the two ethereal oxygen atoms yields two bidentate ligands bound through phenolic and organic imido donors. The cleavage product is produced as two diastereomers which differ in the coordination geometry at the metal. Both isomers have been characterized by X-ray crystal structure determinations. The diastereomeric distribution is determined primarily by the nature of the alcohol employed. The ligand oxidation can be prevented by replacement of the ethylene unit of **1** with the dichlorophenylene moiety of **2**. Osmium complexes of **2** have been produced in oxidation states II, III, IV, VI, and presumably the very rare state V. The apparent osmium(V) complexes are stable but are potent oxidizing agents with potentials for the V/IV couples ranging from ca. 1.31 to 1.65 V vs. NHE. The complex [Os(η^4-CHBA-DCB)(i-Bupy)$_2$]$^+$ forms as an apparent mixture of two diastereomers. The stable osmium(II) complexes of both ligands **1** and **2** are potent reducing agents.

The variety of useful inorganic oxidizing agents presently available is limited by the lack of appropriate oxidation resistant ligands. We have initiated an attempt to prepare a series of strongly oxidizing complexes by designing and synthesizing new oxidation-resistant ligands. Most suitable known ligands are monodentate species in which the donor atom is electronegative (e.g., O^{2-}, Cl^-, F^-). Noteworthy exceptions include the η^2-peroxo and η^4-porphyrinato dianionic ligands.[2,3] Our approach has been to prepare multianionic chelating ligands that are capable of forming stable strongly oxidizing complexes and to investigate the coordination chemistry of the ligands and the reaction chemistry of their metal complexes. Many classical oxidizing agents (e.g., CrO_3, $KMnO_4$) exhibit poor chemoselectivity when oxidizing organic substrates. For some reactions a fundamental reason for this behavior is that additional metal-based oxidizing agents are formed during the redox process which oxidize the organic substrate in a manner different from the initial oxidizing agent. An example is the chromic acid oxidation of cyclobutanol in which chromium(VI) cleanly oxidizes cyclobutanol to cyclobutanone, but the chromium(IV) generated in this process also attacks the cyclobutanol and produces ring cleavage. The final inorganic product is chromium(III).[4] We believe that in searching for selective transition-metal oxidizing agents it is highly desirable to seek or design systems which allow one to *control oxidation state changes* at the metal site during an oxidation process. In particular, we wish to generate complexes that will undergo a single oxidation reaction with a specific organic substrate to give a

(1) Myron A. Bantrell Research Fellow, 1981–1983, the California Institute of Technology.

(2) For recent examples of the use of highly oxidized porphyrin complexes in oxidation reactions see: (a) Groves, J. T.; Watanabe, Y.; McMurry, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4489. (b) Groves, J. T.; Takahashi, T. *Ibid.* **1983**, *105*, 2073. (c) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *Ibid.* **1983**, *105*, 3510. (d) Smegal, J. A.; Hill, C. L. *Ibid.* **1983**, *105*, 3515.

(3) The extremely oxidized complexes [Fe(bpy)$_3$]$^{4+}$ and [Ru(bpy)$_3$]$^{4+}$ have recently been produced electrochemically in liquid SO_2 showing that aromatic ligands are capable of forming observable complexes that are potent oxidizing agents. Gaudiello, J. G.; Sharp, P. R.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373. Stable very highly oxidizing complexes have recently been reported. Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689.

(4) Benson, D. "Mechanisms of Oxidation by Metal Ions"; Elsevier: New York, 1976, pp 178–193.

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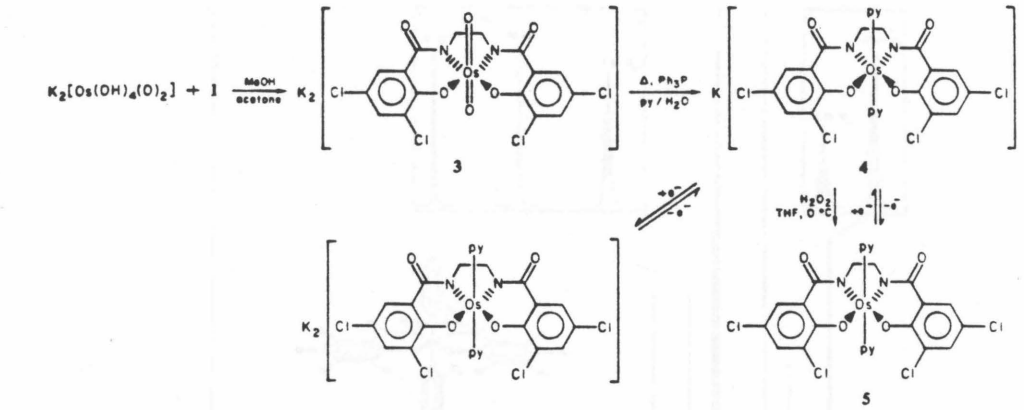
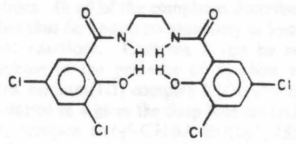
Scheme I



nonactive reduced inorganic product. Multianionic chelating ligands might provide the stabilization of the reduced inorganic product that is necessary for the achievement of this goal.

An important primary goal in our work has been to define the necessary structural features that make a multianionic chelating ligand compatible with very oxidizing metal centers and the environment necessary to generate them. These features include (i) resistance to oxidation, (ii) the formation of five- and six-membered metallacycles upon coordination, (iii) negative charge sufficient to counter the positive charge of the metal center, (iv) chemically innocent binding sites that are resistant to hydrolysis and other displacement reactions, (v) ease of derivatization to vary the oxidizing power of the complex and to incorporate steric bulk or chiral centers to achieve regio-, enantio-, and stereoselective transformations, and (vi) convenient syntheses that will facilitate the use of interesting complexes. The complexes may need to be coordinatively unsaturated to allow the substrate to coordinate prior to oxidation or to facilitate reactions which expand the coordination shell such as β-hydrogen transfer.

Two ligands that have been designed and examined as possible candidates are the potentially tetradentate, tetraanionic ligands H_4CHBA-Et (**1**) and H_4CHBA-DCB (**2**).[5,6] Note that these



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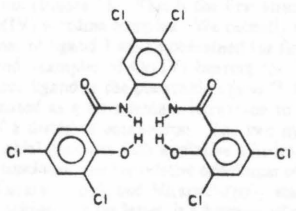


2

(5) Ligand names are 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane, H_4CHBA-Et (**1**); 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene, H_4CHBA-DCB (**2**); 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-ethylene, H_4CHBA-ethylene; 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-*trans*-1,2-dimethoxyethane, H_4CHBA-*t*-1,2-diMeO-Et; *N*-formyl-3,5-dichloro-2-hydroxybenzamide, H_2Fo-CHBA. Abbreviations: py = pyridine; *t*-Bupy = 4-*tert*-butylpyridine; bpy = 2,2'-bipyridine; Ph_3P = tripbenylphosphine; *t*-BuNC = *tert*-butyl isocyanide; TFA = trifluoroacetic acid; BPG = basal plane pyrolytic graphite; TBAP = tetrabutylammonium perchlorate; H_2OEP = octaethylporphyrin; SCE = saturated calomel electrode.

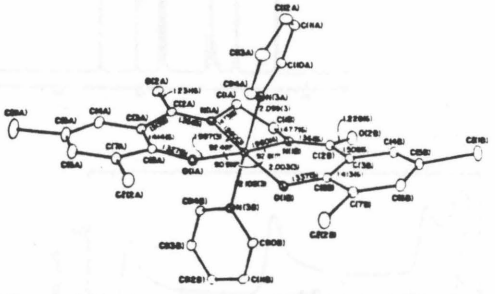


Figure 1. Molecular structure of Os(η^4-CHBA-Et)(py)$_2$ (**5**).

ligands contain organic amide functional groups which when N-coordinated are known to shift formal potentials of metal complexes to less positive values, i.e., to stabilize the higher oxidation state.[7-9] The chlorine substituents were introduced to protect the aromatic rings from oxidation.

Here we report that it is possible to coordinate **1** and **2** as tetradentate tetraanions to osmium and that stable highly reducing complexes of **1** and **2** and highly oxidizing complexes of **2** can be produced. Osmium complexes in the oxidation states II, III, IV, V, and VI are described. It is shown that **1** and **2** meet the criteria listed above with the exception that **1** is not sufficiently resistant to oxidation to allow formation of a strongly oxidizing complex. The site of oxidative sensitivity in complexes of **1** has been identified as the ethylene unit bridging the two organic amide nitrogens. It is important to note that it is a simple matter to block this oxidation of the ligand by replacing the ethylene group with the more robust dichlorophenylene unit of **2**. Osmium is a particularly useful test metal since complexes in several of the higher oxidation states yield readily observable NMR spectra, a pleasant contrast with other metals we have investigated. This has proved

(6) (a) **1** forms a dimeric complex with chromium(III) in which both N-bound and O-bound organic amide ligands are found. Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 681. (b) Coordination of **1** as a tetradentate tetraanion to osmium(IV) has been reported. Christie, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1984**, 198.

(7) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385.

(8) The use of multianionic chelating ligands containing organic amide functional groups to stabilize Cu(III) and Ni(III) has been extensively studied. (a) Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23. (b) Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021. (c) Kimura, E.; Sakonaka, A.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1982**, *104*, 4255.

(9) (a) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1166. (b) Fabbrizzi, L.; Perotti, A.; Poggi, A. *Inorg. Chem.* **1983**, *22*, 1411.

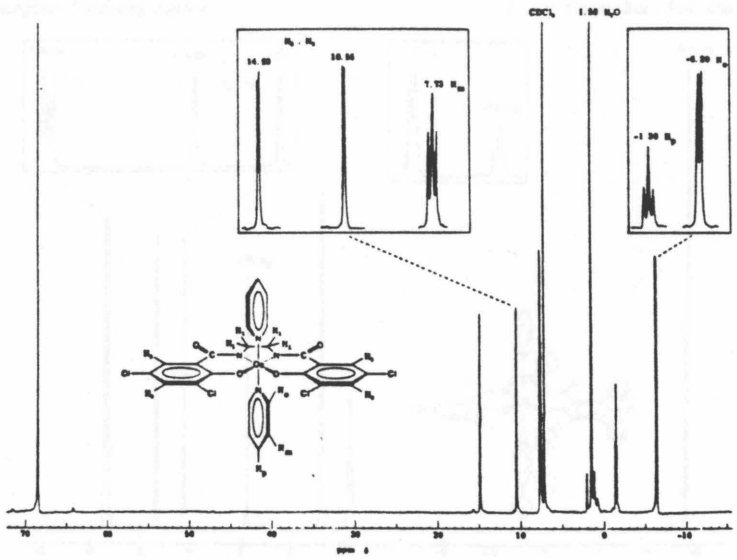


Figure 2. 90-MHz ^{1}H NMR spectrum of **5** ($CDCl_3$).

indispensible in characterizing the complexes described here.

Results and Discussion

Synthesis and Oxidation of an Os(IV) Complex of Ligand 1. The ligands **1** and **2** can be synthesized in high yields from readily available starting materials and familiar organic reactions. Osmium insertion into **1** can be achieved quantitatively as shown in Scheme I. The orange osmium(VI) complex $K_2[Os(\eta^4\text{-CHBA-Et})(O)_2]$ (**3**) contains trans-oxo ligands, as established by IR. Like other d^2 trans-dioxo osmium(VI) complexes this material is diamagnetic[10] and provides a reference for NMR spectroscopy. The IR and ^{1}H NMR data require equatorial coordination of the ligand **1** as a tetradentate tetraanion. Once bound in this fashion the ligand remains coordinated through a variety of chemical transformations. In all of the complexes described in this paper the ligand has thus far shown no sensitivity to hydrolysis or other displacement reactions. Complex **3** can be reduced by triphenylphosphine in the presence of pyridine to produce the paramagnetic osmium(III) complex $K[Os(\eta^4\text{-CHBA-Et})(py)_2]$ (**4**), and oxidation of **4** gives the deep blue neutral paramagnetic osmium(IV) complex $Os(\eta^4\text{-CHBA-Et})(py)_2$ (**5**) in high yield.

Complex **5** has been characterized by an X-ray crystal structure determination (Figure 1). This is the first structural study of an osmium(IV) pyridine complex. We recently reported on an Os(IV) dimer of ligand **1** which contained the first structurally characterized examples of Os(IV) bearing the N-coordinated organic amido ligand or the phenoxide ligand.[6b] In **5** the ligand **1** is coordinated as a tetradentate tetraanion to the equatorial positions of a distorted octahedron. The two pyridine ligands occupy the axial positions with a relative dihedral angle of 73°. It has been concluded that the relative orientation of *trans*-pyridine ligands in $Co(acac)_2(py)_2$ and $Ni(acac)_2(py)_2$, staggered for the former and eclipsed for the latter, is a function of crystal packing effects.[11] The paramagnetic complex **5** exhibits a well-resolved ^{1}H NMR spectrum as shown in Figure 2. Spectra of this type have been previously observed for osmium(IV) complexes.[12] The signal for the bridging ethylene protons is a singlet at 68.55 ppm.

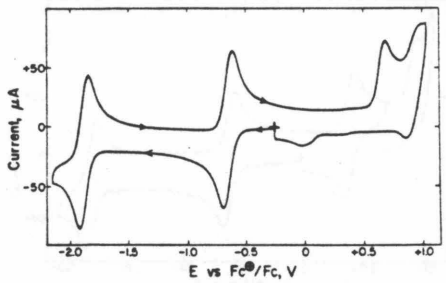


Figure 3. Cyclic voltammogram of 1 mM **5** in CH_2Cl_2, 0.1 M TBAP at 0.174 cm^2 BPG electrode. Scan rate = 200 mV s^{-1}.

The aromatic protons of the chelate are found at 14.92 (d, 2 H, $^4J_{(H-H)}$ = 3 Hz) and 10.54 ppm (d, 2 H, $^4J_{(H-H)}$ = 3 Hz). The signals for the pyridine ortho and para protons are shifted upfield from the normal diamagnetic range (H_o, −6.29, d, 4 H, $^3J_{(H-H)}$ = 8 Hz; H_p, −1.39, t, 2 H, $^3J_{(H-H)}$ = 8 Hz), whereas the signal for the meta protons is not significantly affected (H_m, 7.72, t, 4 H, $^3J_{(H-H)}$ = 8 Hz). It is probable that the magnitude of the paramagnetic contact shift of the pyridine signals is directly related to the nature of the second LUMO of pyridine, $3B_1$, which is composed of p orbitals on nitrogen and on the ortho and para positions, but not the meta positions.[13]

Cyclic voltammetry was used to probe the redox chemistry of the new complexes and the oxidative stability of the coordinated ligands. A typical cyclic voltammogram of **5** (1 mM in CH_2Cl_2, 0.1 M TBAP[5]) at a BPG[5] electrode is shown in Figure 3. Potentials were measured against the ferrocinium/ferrocene (Fc^+/Fc) couple which we have consistently measured as ca. 0.48 V vs. SCE[5] in the same medium. Two reversible diffusion-controlled one-electron responses having formal potentials of −0.65 and −1.88 V are found. In addition, two irreversible responses appear at E_p = +0.70 V and ca. 1.00 V. Plots of peak current vs. the square root of scan rate rate over the range 20–500 mV s^{-1} are linear for the two reversible couples and the first oxidation, indicating

(10) Schroeder, M. *Chem. Rev.* **1980**, *80*, 187.
(11) Elder, R. C. *Inorg. Chem.* **1968**, *7*, 1117; **1968**, *7*, 2316.
(12) (a) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417. (b) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636. (c) Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867.

(13) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; p 265.

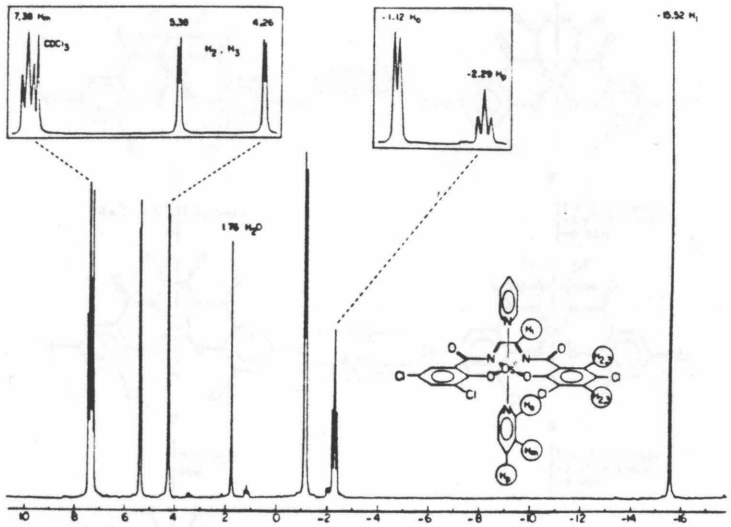


Figure 4. 90-MHz ^1H NMR spectrum of **7** ($CDCl_3$).

diffusion control. Controlled potential reduction of **5** at −0.90 V consumes one electron per molecule and produces **4** which can be reoxidized to pure **5**. Reduction of **5** in acetonitrile at −2.10 V consumes two electrons per molecule and produces a purple solution of the corresponding osmium(II) complex that is stable under an inert atmosphere. Exposure to air causes rapid formation of **4**. The formal potential of the osmium(III/II) couple, $[Os(\eta^4\text{-CHBA-Et})(py)_2]^{-/2-}$, −1.88 V, is almost 2 V more negative than that of the corresponding porphyrin complex, $[Os(\eta^4\text{-OEP})(py)_2]^{+/0}$, (0.0 V), in the same medium.[5,14] The osmium(II) complex $[Os(\eta^4\text{-CHBA-Et})(py)_2]^{2-}$ is thus a very powerful reducing agent. Clearly the tetraanionic ligand stabilizes osmium(III) much more strongly than does the dianionic octaethylporphyrinato ligand. We anticipate that this superior stabilization capacity will be a general property of the tetraanions.

The oxidative sensitivity of the ethylene unit bridging the amide nitrogens causes the oxidation of complex **5** to be irreversible. Electrochemical oxidation of **5** at 0.87 V in dichloromethane containing ROH (R = alkyl, H) (0.5 mol per mmol of osmium) consumes at least six electrons per osmium atom and gives quantitative conversion of **5** to either one of two new complexes, **9** and **9′**, or a mixture of both depending on the nature of R, vide infra (Scheme II). Thin-layer chromatography (TLC) of the anolyte solution monitored during the course of the electrolysis shows that the conversion proceeds through three distinct intermediates—**6**, **7**, and **8**. Comparison of TLC measurements when different alcohols are employed indicates that **6** and **8** contain the alcohol group while **7**, **9**, and **9′** do not. We wished to understand these transformations for two reasons. First, there is an obvious connection between the goals mentioned in the introduction and a knowledge of any oxidative reactions of a complex of the new ligand **1**. Second, it is possible to convert **9** and **9′** to active catalysts for electrooxidation of alcohols, and our studies of these catalytic systems required a knowledge of the structures of possible participant complexes.

It was inconvenient to separate and isolate the complex mixtures of osmium compounds that form during the electrolysis. Accordingly we sought separate chemical syntheses of the various intermediates and discovered that compound **7** can be quantitatively produced by autoxidation of **5** adsorbed on silica gel (Scheme II). The structure of **7** has been established by ^1H NMR (Table I and Figure 4) and ^{13}C NMR (Table II).[15] The signal for the

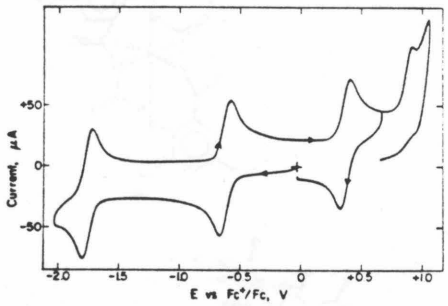
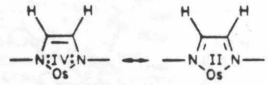


Figure 5. Cyclic voltammogram of 1 mM **7** in 0.1 M TBAP/CH_2Cl_2 at 0.174 cm^2 BPG electrode; scan rate = 200 mV s^{-1}.

methylene protons of the metallacyclopentane ring of **5** is found at 68.55 ppm, whereas the signal for the metallacyclopentene ring methine protons of **7** is found at −15.52 ppm. The five-membered

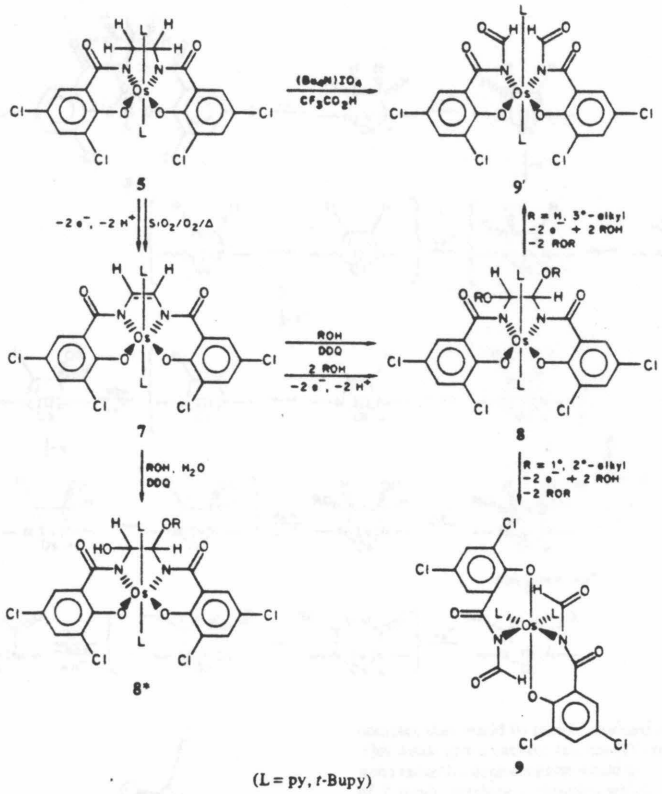


unsaturated metallacycle of **7** can be represented by two contributing resonance structures in which the formal oxidation state of the metal is different. The cyclic voltammogram of **7** in the absence of alcohol is shown in Figure 5. Three reversible diffusion-controlled one-electron waves are found at E^f = −1.76, −0.62, and 0.37 V, and an irreversible oxidation is found at E_p = 0.92 V. The oxidation of **7** at 0.37 V is reversible in the absence of alcohols, but it becomes irreversible at low scan rates if alcohol is present. Electrochemical oxidation of **7** at 0.87 V in the presence of alcohol or water produces **8** and then **9** and/or **9′**. Complex

(14) Brown, G. M.; Hopf, F. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 5385.

(15) A considerable number of ligand oxidative dehydrogenations have been previously reported. For examples of such reactions in osmium chemistry see: Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6161 and references therein. Oxidation of methylene units attached to the nitrogen atoms of chelating N-coordinated polypeptides to copper(III) has been reported. Rybka, J. S.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1453 and references therein. For a recent review of α,α-diimine complexes including ligand oxidations see: Van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

Scheme II



(L = py, *t*-Bupy)

6 is produced in very small concentrations as an intermediate in the electrooxidation of **5**, but not **7**. We have not been able to isolate and characterize this compound.

Chemical conversion of **7** to **8** can be effected in high yield by oxidation with dichlorodicyanobenzoquinone (DDQ) in dichloromethane in the presence of alcohol or water (Scheme II). The five-membered metallacycle in **8** is symmetrically substituted by *trans*-alkoxide groups, but if the oxidation with DDQ is performed in the presence of both alcohol and water the unsymmetrically substituted complex **8°** bearing *trans*-alkoxide and hydroxide groups is produced in addition to the two symmetrical complexes **8** (R = H or alkyl). Complex **8°** forms in very small concentrations in the electrooxidation process when alcohols are used implying the presence of small quantities of water. The structures of these complexes have been confirmed by ^1H and ^{13}C NMR (Tables I and II). The ^1H NMR spectrum of **8°** shows the multiplicity of signals expected for two inequivalent pyridines and two inequivalent rings in the chelate ligand. For compounds **7** and **8** an alternative structure which would also satisfy the accumulated spectroscopic data involves axial phenoxide ligands with the nitrogen donors in the equatorial plane and the pyridine ligands in a cis configuration. However, this structure would probably be highly strained.

Electrochemical oxidation of **8** at 0.87 V in the presence of alcohol or water results in cleavage of the carbon–carbon bond of the five-membered metallacycle and dealkylation or deprotonation of the oxygen substituents to afford the two diastereomeric complexes **9** and **9′** which differ in cis–trans ligand relationships only. Both complexes with L = *t*-Bupy have been characterized by X-ray crystal structure determinations (see Figure 6 for **9** and Figure 7 for **9′**). These are the first structurally characterized N-coordinated organic imido complexes of osmium. The diastereomeric composition is a function of the R group and the ligand L. For L = py the transformations are 100% stereoselective. When R is methyl, ethyl, *n*-butyl, isopropyl, or benzyl, **9** is the sole product and is formed quantitatively. When R is *tert*-butyl, *tert*-amyl, or H, **9′** is the quantitative product. It was not possible

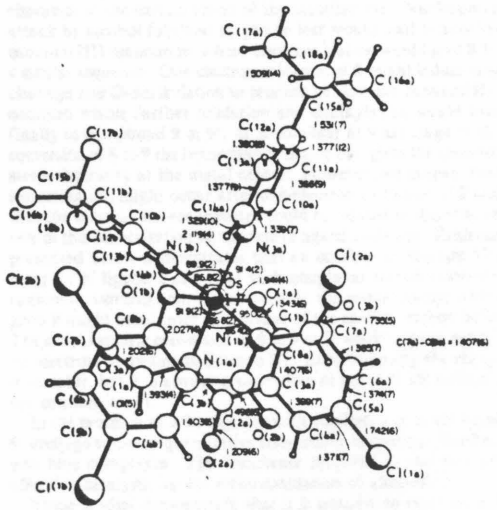
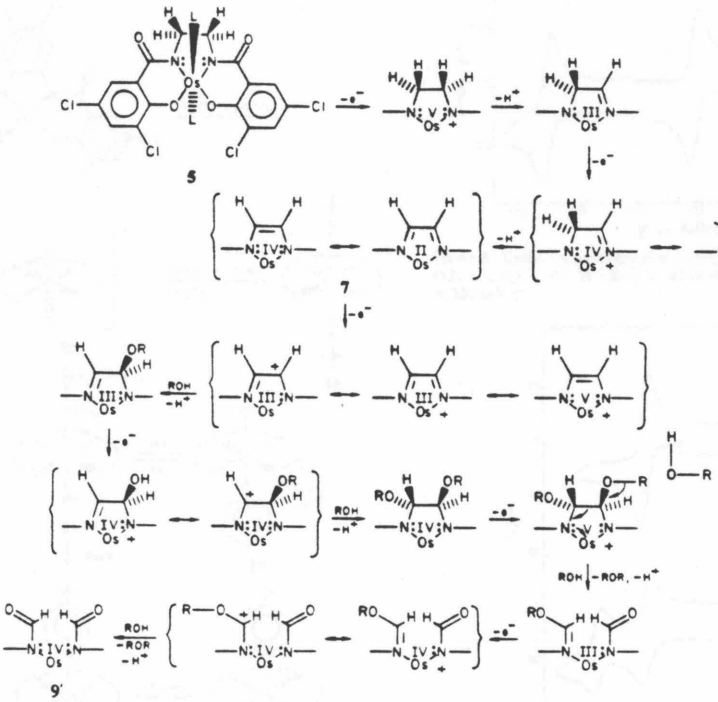


Figure 6. Molecular structure of $Os(\eta^2\text{-Fo-CHBA})_2\text{-}cis\text{-}(t\text{-Bupy})_2$ (**9**).

Scheme III



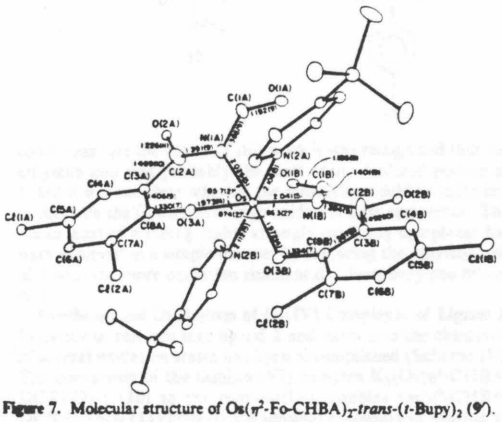


Figure 7. Molecular structure of $Os(\eta^2\text{-Fo-CHBA})_2$-*trans*-(*t*-Bupy)$_2$ (**9′**).

to grow crystals suitable for structural analysis with L = py for either diastereomer. Consequently, the entire series of complexes was synthesized with L = *t*-Bupy. This substitution causes a change in the diastereomeric distribution of **9** and **9′**. Thus the electrooxidation of **5** (L = *t*-Bupy) in the presence of isopropyl alcohol produces a mixture of **9** and **9′** in the approximate ratio 7:3. Compound **9′** can also be produced as the sole product by oxidation of **5** in dichloromethane with tetrabutylammonium periodate in the presence of excess trifluoroacetic acid (TFA). **9** and **9′** have been characterized by NMR (Tables I and II).

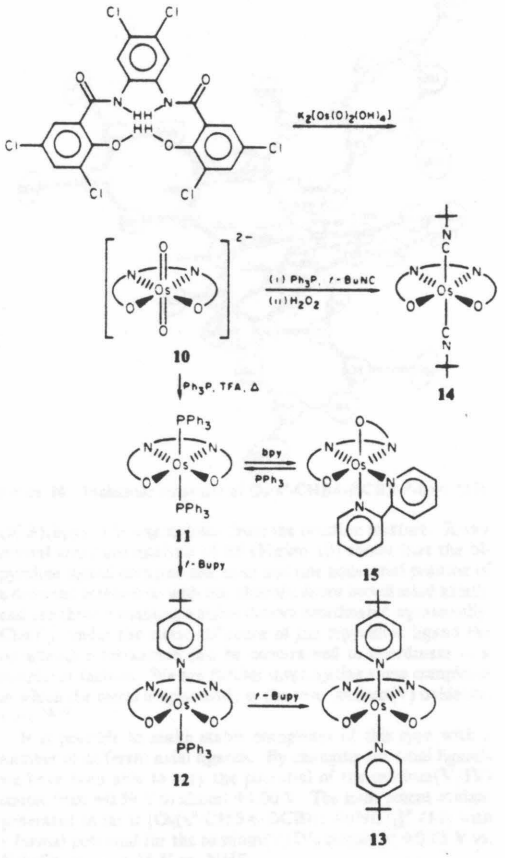
At this juncture it might be helpful to suggest a mechanism for the combination of ligand and metal oxidations that we have described (Scheme III). One-electron oxidation of **5** might afford an osmium(V) complex which could undergo spontaneous reductive deprotonation to produce an osmium(III) monoimine complex that would be rapidly oxidized at the potential employed. This would give a cationic osmium(IV) monoimine complex which upon reductive deprotonation would give **7**. One-electron oxidation of **7** would produce a complex which possesses carbonium ion character at the carbon atoms of the metallacycle. Nucleophilic attack by alcohol followed by proton loss would lead to another osmium(III) monoimine whose electrooxidation would give **8** by a similar sequence. One-electron oxidation of **8** might induce ring cleavage and O-dealkylation to produce yet another osmium(III) complex whose further oxidation and dealkylation would lead finally to compound **9** or **9′**. It is not clear at what stage in the conversion of **8** to **9** the isomerization occurs that gives the observed stereochemistry at the metal center. However, we suspect that isomerization might occur after one-electron oxidation of **8** and that the unusual stereochemistry could be related to the relative rate of this isomerization vs. the rate of ligand oxidation. Evidence presented below demonstrates that an octahedral osmium(IV) complex of ligand **2** can exist with nonplanar tetradentate tetraanionic coordination. Consequently, the isomerization which gives **9** might occur prior to cleavage of the carbon–carbon bond. The stoichiometric conversion of **5** to **9** or **9′** would require exactly six electrons according to Scheme III. Experimentally the charge is variable, but it is always greater than or equal to six electrons per osmium atom.

In the presence of acid together with an alcohol or water **9** and **9′** undergo two-step quantitative conversions to produce two final new blue complexes. The complexes prepared in this way are effective catalysts for the electrooxidation of alcohols.[16]

These studies demonstrate that it is possible to coordinate **1** as a nonlabile tetradentate tetraanion to osmium and that this type of coordination results in a significant stabilization of higher oxidation states. However, the ethylene unit of **1** is an unsuitable feature for ligands that are designed to resist strongly oxidizing

(16) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Krafft, T. E., manuscript in preparation.

Scheme IV



conditions. At the outset of this work it was recognized that the ethylene unit was probably the most easily oxidized portion of **1**, but it was not clear whether the sensitivity would be sufficient to preclude the formation of high oxidation state complexes. The major goal of building stable strongly oxidizing complexes has been achieved in a simple manner by replacing the ethylene unit of **1** with the more oxidation resistant dichlorophenylene bridge of **2**.

Syntheses and Oxidations of Os(IV) Complexes of Ligand 2. Insertion of osmium into ligand **2** and entry into the chemistry of several oxidation states has been accomplished (Scheme IV). The conversion of the osmium(VI) complex $K_2[Os(\eta^4\text{-CHBA-DCB})(O)_2]$ (**10**) to the osmium(IV) complex $Os(\eta^4\text{-CHBA-DCB})(PPh_3)_2$ (**11**) involves the unusual procedure of heating **10** under reflux in a triphenylphosphine/TFA solution. The reaction affords **11** in high yield. Compound **11** is a very versatile intermediate for ligand exchange reactions at osmium(IV), as illustrated in Scheme IV. The compounds shown in Scheme IV have been characterized by ^1H NMR (Table I).

The cyclic voltammogram of $Os(\eta^4\text{-CHBA-DCB})(t\text{-Bupy})_2$ (**13**) is shown in Figure 8. The irreversible response observed upon oxidation of complex **5** (Figure 3) has been converted to a reversible couple at $E^f = +0.70$ V. Bulk electrolysis of dark blue **13** at 1.0 V in dichloromethane consumes one electron per osmium atom and produces a purple solution which apparently contains an equimolar mixture of two osmium(V) complexes. The cyclic voltammogram after electrolysis still contains the original reversible couple arising from **13**, but the peak currents are only about half as large as they were originally. In addition, two new couples

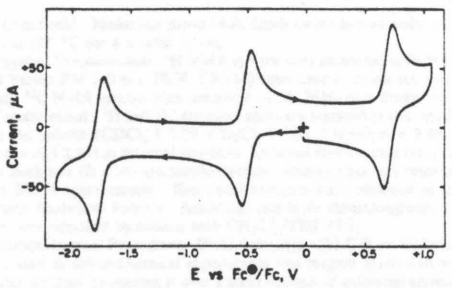


Figure 8. Cyclic voltammogram of 1 mM $Os(\eta^4\text{-CHBA-DCB})(t\text{-Bupy})_2$ (**13**) in CH_2Cl_2, 0.1 M TBAP at 0.174 cm^2 BPG electrode. Scan rate = 200 mV s^{-1}.

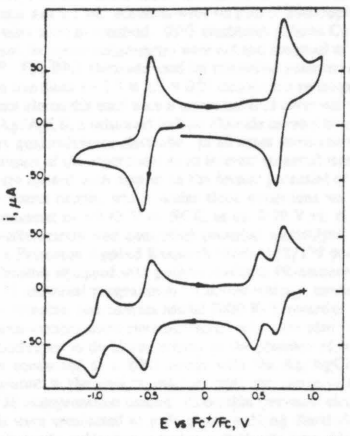


Figure 9. Cyclic voltammogram of (a, top) 1 mM $Os(\eta^4\text{-CHBA-DCB})(t\text{-Bupy})_2$ (**21**) + 0.1 M TBA-BF_4 in CH_2Cl_2 and (b, bottom) 1 mM $[Os(\eta^4\text{-CHBA-DCB})(t\text{-Bupy})_2]^+$ + 0.1 M TBA-BF_4 in CH_2Cl_2; one-electron reduction restores cyclic voltammogram (a). Pt wire electrode; 200 mV s^{-1}.

appear several hundred millivolts negative and with peak currents also about half as large as the original couples (Figure 9). The open circuit potential of the electrode is positive of all of the couples showing that all of the original osmium(IV) complex has been oxidized. One-electron reduction of the mixture restores a pure solution of **13**. We suspect that the oxidation products are a mixture of geometrical isomers.

A change to nonplanar coordination of the tetradentate tetraanion in **13** upon one-electron oxidation could give rise to an equilibrium mixture of diastereomers. The complex $Os(\eta^4\text{-CHBA-DCB})(PPh_3)_2$ (**11**) which contains *trans*-phosphine ligands might be expected to resist this isomerism since it would require cis coordination of the bulky phosphine ligands. Bulk electrolysis of **11** in acetonitrile at 0.86 V involves one electron per osmium atom and produces a dark green solution of what we assume to be the osmium(V) complex $[Os(\eta^4\text{-CHBA-DCB})(PPh_3)_2]^+$. This oxidized material exhibits no additional waves in the cyclic voltammogram.[17] In order to test the ability of ligand **2** to assume a nonplanar geometry, complex **11** was treated with 2,2′-bipyridine in toluene under reflux and the compound $Os(\eta^4\text{-CHBA-}$

(17) For a recent electrochemical study of the systems $[M(bpy)_2(OH_2)_2]^{2+}$ (M = Ru, Os) see: Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407. For the osmium case stable complexes were found for oxidation states II, III, IV, V, and VI with a small variation in $E_{1/2}$ values, Os(III/II) = +0.16 V (SSCE), Os(VI/V) = +0.82 V. Oxidation is accompanied by deprotonation. For a recent electrochemical study of some osmium(IV) and (VI) complexes see: Armstrong, J. E.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1545.

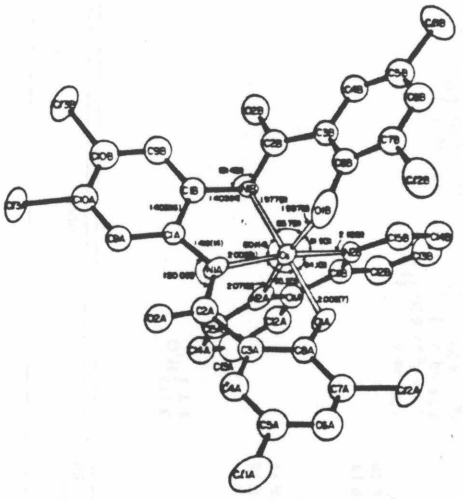


Figure 10. Molecular structure of Os(η^4-CHBA-DCB)(η^2-bpy) (**15**).

DCB)(bpy) (**15**) was isolated from the reaction mixture. X-ray crystal structure analysis of **15** (Figure 10) shows that the bipyridine ligand occupies one axial and one equatorial position of a distorted octahedron with one phenolic donor coordinated axially and the three remaining anionic donors coordinated equatorially. Clearly, under the steric influence of the bipyridine ligand the tetradentate tetraanion can be constrained to coordinate in a nonplanar fashion. We are further investigating these complexes in which the metal is apparently in the rare osmium(V) oxidation state.[18,19]

It is possible to make stable complexes of this type with a number of different axial ligands. By changing the axial ligands we have been able to vary the potential of the osmium(V/IV) couple from +0.59 V to almost +1.00 V. The most potent oxidant generated so far is [Os(η^4-CHBA-DCB)(*t*-BuNC)$_2$]$^+$ (**14**) with a formal potential for the osmium(V/IV) couple of +0.93 V vs. Fc^+/Fc, or ca. 1.65 V vs. NHE.

The results we have presented demonstrate the versatility of ligands such as [η^4-CHBA-Et]$^{4-}$ and [η^4-CHBA-DCB]$^{4-}$ in the formation of both highly oxidizing and highly reducing inorganic complexes. A set of ligand design features that are important in the preparation of stable complexes has been identified. We believe that chelate complexes of this class of ligands will find application in selective redox reactions, and we are actively pursuing such studies with a number of metals and oxidation reactions.

Experimental Section

Materials. All solvents were reagent grade (Aldrich, Baker Mallinckrodt, M.C.B. or U.S.I.) and were used as received unless otherwise noted. Acetic anhydride (reagent, Mallinckrodt), 2-acetylsalicylic acid (Aldrich), 2,2′-bipyridine (99.5%, Aldrich), *tert*-butyl isocyanide (>98%, Fluka), 4-*tert*-butylpyridine (99%, Aldrich), Cl_2 (Matheson), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (98%, Aldrich), 3,5-dichlorosalicylic acid (Pfaltz and Bauer), glacial acetic acid (Aldrich), $HClO_4$ (60%, Mallinckrodt), H_2O_2 (30% Superoxol, Baker), KOH (reagent, Baker), OsO_4 (99.8%, Alfa), H_3PO_4 (85%, Baker), pyridine (reagent, Mallinckrodt), triethylamine (reagent, M.C.B.), trifluoroacetic acid (reagent, M.C.B.), and triphenylphosphine (99%, Aldrich) were all used as received. The oxalyl chloride and ethylenediamine (Aldrich) used in the ligand syntheses were both freshly distilled. 4,5-Dichloro-*o*-phenylenediamine was dried over Na_2SO_3 and recrystallized from hexane. Silica gel was 60–200 mesh (Davidson). Analytical and preparatory thin layer chromatography plates, 250 and 1000 μm, respectively, were silica gel GF (Analtech). Molecular sieves (4 Å, Linde) were heated under vacuum at 300 °C for 4 h prior to use.

Physical Measurements. ^1H NMR spectra were measured at 90 MHz on a Varian EM 390 or a JEOL FX90-Q spectrometer unless otherwise noted. ^{13}C NMR spectra were measured at 500 MHz on a Bruker WM 500 spectrometer. ^1H and ^{13}C chemical shifts are reported in δ vs. Me_4Si with the solvent ($CDCl_3$ δ 7.25, CD_2Cl_2 δ 5.35, Me_2SO-d_6 δ 2.50 or acetone-d_6 δ 2.05) as internal standard. Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer. Raman data was recorded on a SPEX spectrometer. Elemental analyses were obtained at the Caltech Analytical Facility. Analytical thin layer chromatography results were obtained by elution with CH_2Cl_2/THF (9:1).

Electrochemical Procedures. Dichloromethane (M.C.B. or Mallinckrodt) used in electrochemical experiments was reagent grade and was further purified by passing it over a short column of activated alumina (Woelm N. Akt. I). Acetonitrile (Burdick and Jackson, distilled in glass) was dried over 3-Å molecular sieves. TBAP supporting electrolyte (Southwestern Analytical Chemicals) was dried, recrystallized twice from acetone/ether, and then dried under vacuum. The TBAP concentration in all solutions was 0.1 M. Alcohols were reagent or spectrophotometric grade and were used as received. BPG electrodes (Union Carbide Co., Chicago) used for cyclic voltammetry were cut and mounted as previously described.[20] The BPG electrode used for controlled potential oxidations was cut as a thin sheet (~1.7 × 4.5 × 0.07 cm) from a rectangular block. The reference electrodes used were a saturated KCl silver–silver chloride electrode (Ag/AgCl), a saturated sodium chloride calomel electrode, and a silver wire quasireference electrode. In all cases ferrocene was added at the conclusion of the experiment as an internal potential standard. All potentials are quoted with respect to the formal potential of the ferrocinium/ferrocene couple, which under these conditions we have consistently measured as +0.48 V vs. SCE, or ca. 0.70 V vs. NHE.

Cyclic voltammetry and controlled potential electrolysis were performed on a Princeton Applied Research Model 173/179 potentiostat/digital coulometer equipped with positive feedback IR-compensation and a Model 175 universal programmer. Current–voltage curves were recorded on a Houston Instruments Model 2000 X–Y recorder. Standard two- and three-compartment electrochemical cells were used. Controlled potential oxidations in dichloromethane in the presence of water or alcohol were conducted at a BPG anode with the Ag/AgCl reference electrode placed in the anolyte solution near the anode to reduce the amount of IR-compensation needed. Controlled potential electrolyses in acetonitrile were conducted at a Pt gauze working electrode with the reference electrode isolated in a separate compartment. These experiments were performed in a helium atmosphere dry box (Vacuum/Atmospheres Co.).

X-ray Data Collection and Structure Determination of 5. A suitable crystal was obtained by slow crystallization from THF/water. Oscillation and Weissenberg photographs showed symmetry no higher than $\bar{1}$. The intensity data were collected on a locally modified Syntex $P2_1$ diffractometer with graphite monochromator and Mo Kα radiation (λ 0.7107 Å). Unit cell parameters (Table IV) from least-squares refinement of $\sin^2\theta$ based on fifteen 2θ values, each 2θ an average of four values ($\pm 2\theta$, $\pm\omega$, φ, χ; $\pm 2\theta$, $\pm\omega$, $\pi + \varphi$, $\pi - \chi$). The three check reflections indicated no decomposition and the data were reduced to F_o^2; the variances of the intensities were obtained from counting statistics with an additional term (0.02 × scan counts).[2] The form factors were taken from ref 21.

The Os atom coordinates were derived from a Patterson map, and successive electron density maps revealed the remaining atoms. Hydrogen atoms were introduced into the model at idealized positions with fixed $U = 0.063$ Å^2. Several cycles of least-squares refinement, minimizing $\sum w\Delta^2$, with $w = \sigma^{-2}(F_o^2)$ and $\Delta = F_o^2 - (F_c/k)^2$, resulted in $S = 1.92$ and $R_F = 0.034$.[22] The final value for the isotropic extinction coefficient was 0.396 (36) × 10^{-6}. The calculations were carried out on a Vax 11/780 with the CRYM system of programs.[23]

X-ray Data Collection and Structure Determination of 9. A long crystal of **9** (L = *t*-Bupy) was obtained by slow crystallization from CH_2Cl_2/hexane. Diffractometer data (Nicolet diffractometer, graphite monochromator, Mo Kα radiation) indicated monoclinic symmetry and space group $C2/c$ (Table IV). The six check reflections indicated no decomposition, and following an empirical correction for absorption, the data were reduced to F_o^2.

(18) "Gmelin Handbuch der Anorganischen Chemie"; Osmium Supplement; Springer-Verlag: New York, 1980; Vol. 1.
(19) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; 4th ed.; John Wiley and Sons: New York, 1980; pp 912–933.
(20) Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1979**, *101*, 3450.
(21) Atomic scattering factors were taken from: "International Tables for X-ray Crystallography"; Witton: Birmingham, 1974; Vol. IV, pp 72–97.
(22) The goodness-of-fit $S = [\sum w\Delta^2/(n-v)]^{1/2}$, n = number of reflections, v = number of parameters; $R_F = \sum||\Delta F|/\sum|F_o|$ (based on reflections with $I > 0$), $\Delta F = |F_o| - |F_c|$, $R_F = R_F$ (based on reflections with $I > 3\sigma_I$).
(23) The CRYM computing system was used (D. J. Duchamp, California Institute of Technology).

Table I. 90-MHz ^{1}NMR Data for All Osmium Complexes[a]

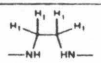
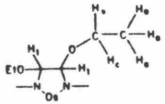
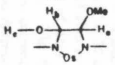
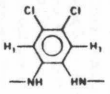
no.	compd	chelate ligand H_1	chelate ligand H_2, H_3[b]		pyridine H_o	pyridine H_m	pyridine H_p	pyridine t-Bu	other
1[c]		3.70 s, 4	7.54 d, 2	7.74 d, 2					
3[d]		3.88 s, 4	7.27 d, 2	8.21 d, 2					3.77, s, 2 } H_2O
5[e]	L = py	68.55 s, 4	10.55 d, 2	14.93 d, 2	−6.29, d, 4 $J_{o,m}$ = 8 Hz	7.73, dd, 4 $J_{m,o}$ = 8 Hz $J_{m,p}$ = 8 Hz	−1.39, t, 2 $J_{p,m}$ = 8 Hz		
5[e]	L = t-Bupy	69.78 s, 4	10.78 d, 2	15.40 d, 2	−7.26, d, 4 $J_{o,m}$ = 7.5 Hz	7.38, d, 4 $J_{m,o}$ = 7.5 Hz		0.18 s, 18	
7[e]		−15.52 s, 2	4.26 d, 2	5.38 d, 2	−1.12, d, 4 $J_{o,m}$ = 8 Hz	7.38, dd, 4 $J_{m,o}$ = 8 Hz $J_{m,p}$ = 8 Hz	−2.29, t, 2 $J_{p,m}$ = 8 Hz		
7[e]	L = t-Bupy	−14.30 s, 2	4.89 d, 2	5.61 d, 2	−2.90, d, 4 $J_{o,m}$ = 7.5 Hz	7.11, d, 4 $J_{m,o}$ = 7.5 Hz		0.13 s, 18	
8a[e,f]		6.01 s, 2	9.22 d, 2	10.48 d, 2	−1.32, dd, 4 $J_{o,m}$ = 7.5 Hz $J_{o,p}$ = 1.5 Hz	8.59, dd, 4 $J_{m,p}$ = 8.5 Hz $J_{m,o}$ = 7.5 Hz	1.61, tt, 2 $J_{p,m}$ = 8.5 Hz $J_{p,o}$ = 1.5 Hz		2.06, dd, 6 $J_{a,b} = J_{a,c}$ = 8 Hz } H_a 7.54, dq, 2 $J_{a,b}$ = 8 Hz } H_c $J_{b,c}$ = 10 Hz } H_b 6.08, dq, 2 $J_{a,c}$ = 8 Hz } H_b $J_{c,b}$ = 10 Hz } H_c
8b[e]		6.77 s, 2	9.43 d, 2	10.91 d, 2	−1.75, d, 4 $J_{o,m}$ = 7.5 Hz	8.60, dd, 4 $J_{m,o}$ = 7.5 Hz $J_{m,p}$ = 7.5 Hz	1.25, t, 2 $J_{p,m}$ = 7.5 Hz		5.77, s, 6 } $-CH_3$
8a[e,g]			14.43 d, 1 10.67 d, 1	12.79 d, 1 10.29 d, 1	−2.59, dd, 2 $J_{o,m}$ = 7.5 Hz $J_{o,p}$ = 1.5 Hz −6.85, dd, 2 $J_{o,m}$ = 7.5 Hz $J_{o,p}$ = 1.5 Hz	8.94, dd, 2 $J_{m,p}$ = 8.5 Hz $J_{m,o}$ = 7.5 Hz 7.83, dd, 2 $J_{m,p}$ = 8.5 Hz $J_{m,o}$ = 7.5 Hz	−0.57, tt, 1 $J_{p,m}$ = 8.5 Hz $J_{p,o}$ = 1.5 Hz −1.00, tt, 1 $J_{p,m}$ = 8.5 Hz $J_{p,o}$ = 1.5 Hz		4.87, s, 3 } $-CH_3$ 8.59, s, 1 } H_a 16.87, d, 1 $J_{c,d}$ = 3 Hz } H_b 7.57, d, 1 $J_{d,c}$ = 3 Hz } H_c
9[e]			7.65 d, 2	9.52 d, 2	5.33, d, 4 $J_{o,m}$ = 7.5 Hz	9.67, d, 4 $J_{m,o}$ = 7.5 Hz		1.67 s, 18	10.44, s, 2 } H_a
9′[e]	L = t-Bupy L = py		7.39 d, 2	8.11 d, 2	5.23, d, 4 $J_{o,m}$ = 8 Hz	9.20, dd, 4 $J_{m,o}$ = 8 Hz $J_{m,p}$ = 8 Hz	6.26, t, 2 $J_{p,m}$ = 8 Hz		7.28, s, 2 } H_a
9′[e]	L = t-Bupy		7.30 d, 2	7.96 d, 2	4.92, d, 4 $J_{o,m}$ = 7.5 Hz	9.08, d, 4 $J_{m,o}$ = 7.5 Hz		1.42 s, 18	7.14, s, 2 } H_a
2[h]		8.12 s, 2	7.87 d, 2	8.10 d, 2					

Table I (*Continued*)

	10^c	9.47	7.40	8.39					
		s, 2	d, 2	d, 2					
	11^e	4.54	8.39	9.33			8.05, m, 12} H_o	7.42, t, 6 } H_p	
		s, 2	d, 2	d, 2			6.95, dd, 12	$J_{p,m}$ = 8 Hz	
							$J_{m,o} = J_{m,p}$ = 8 Hz } H_m		
	12^f	5.60	9.31	11.64	−2.66, d, 2	7.48, d, 2	0.30 9.13, dd, 6	7.29, dd, 6	
		s, 2	d, 2	d, 2	$J_{o,m}$ = 6 Hz	$J_{m,o}$ = 6 Hz	s, 9 $J_{p\text{-}H_o}$ = 13 Hz } H_o	$J_{m,o} = J_{m,p}$ = 8 Hz } H_m	
							$J_{o,m}$ = 8 Hz	7.68, t, 3 H_p	
								$J_{p,m}$ = 8 Hz	
	13^f	7.50	9.78	11.10	−8.48, d, 4	7.96, d, 4	0.07		
		s, 2	d, 2	d, 2	$J_{o,m}$ = 7 Hz	$J_{m,o}$ = 7 Hz	s, 18		
	14^g	8.39	7.43	8.42			1.44 } *t*-BuNC		
		s, 2	d, 2	d, 2			s, 18 }		
	15^g	8.28	7.11	8.20			8.58, d 2 }	7.54, dd, 2 }	
		s, 2	d, 2	d, 2			J = 8 Hz } bpy	J = 8 Hz } bpy	
							7.76, d, 2 }	7.94, dd, 2 }	
							J = 8 Hz	J = 8 Hz	

[a] The chemical shifts of the paramagnetic Os(IV) species are somewhat concentration dependent. The values reported here are uncorrected. [b] $J_{4,3} = J_{3,2}$ = 3 Hz. [c] δ in acetone-d_6. [d] δ in D_2O. [e] δ in $CDCl_3$. [f] Selective ^1H decoupling experiments have confirmed these assignments. [g] H_d readily exchanges on addition of D_2O which causes collapse of the H_c signal to a singlet. [h] δ in $(CD_3)_2SO$. [i] δ in CD_2Cl_2.

Table II. Selected 500-MHz ^{13}C NMR Data

no.	compd	C_1 (proton coupled)	C_1 (H_1 or H_a selectively decoupled)
7^a		105.28, d_1 J_{CH} = 187 Hz	105.28, s
$8a^a$		51.76, d J_{CH} = 160 Hz	51.76, s
9^a	L = *t*-Bupy	196.46, d J_{CH} = 208 Hz	196.46, s

[a] δ in $CDCl_3$.

Table III. Formal Potentials of Os Compounds

compd	III/II[a]	IV/III[a]	V/IV[a,b]
5	−1.88	−0.65	(+0.70)
5, L = *t*-Bupy	−1.96	−0.70	(+0.66)
7	−1.76	−0.62	+0.37[c]
8b	−1.95	−0.64	(ca. +0.9)
9	−1.88	−0.46	*d*
9′	−1.88	−0.39	*d*
11	−1.72	−0.46	+0.59
13	−1.77	−0.51	+0.70
14	−1.05	−0.57	+0.92

[a] Potentials were measured against the Fc^+/Fc couple which we have measured at ca. 0.48 V vs. SCE. [b] Potentials in parentheses are peak potentials of irreversible oxidations. [c] **7** also exhibits an irreversible oxidation at +0.92 V. [d] No oxidations seen at potentials below +1.1 V.

Solution of the structure was by the Patterson map, and refinement was on $|F|$. The solvent molecule, CH_2Cl_2, is disordered, and attempts to model it and refine the remainder of the structure gave R_F = 0.031 and $S' = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$ = 1.60; final average shift/error = 0.02, the maximum deviation in final ΔP map is 0.59 e/Å^3. The data collection and refinement was carried out by Crystalytics Co.

X-ray Data Collection and Structure Determination of 9′. A thin needlelike crystal of **9′** (L = *t*-Bupy) was obtained from a solution of CH_2Cl_2/EtOH. Oscillation and Weissenberg photographs showed symmetry no higher than $\bar{1}$. The unit cell parameters (Table IV) were determined from a refinement using fifteen 2θ values with 25° < |2θ| < 35°, averaged from centered values at both +2θ and −2θ. The intensity data were collected on a locally modified Syntex $P2_1$ diffractometer with graphite monochromator and Mo Kα radiation. The three check reflections indicated no decomposition, and the data were reduced to F_o^2 as above. The form factors of Os and Cl were corrected for anomalous dispersion.

Solution and refinement of the structure proceeded smoothly; the position of the Os atom was derived from the Patterson map, and the Fourier map phased on the Os atom revealed the remainder of the structure. The H atoms were introduced into the model with fixed coordinates at idealized positions (the methyl H atoms from ΔF maps) and fixed Gaussian amplitudes of U = 0.10 Å^2—full-matrix least-squares refinement of the non-H atoms with anisotropic U_{ij}'s with use of all reflections with $I > 0$;[22] final average shift/error = 0.04 in the last cycle, and the maximum deviation in the final $\Delta\rho$ map of 2.5 e/Å^3.

X-ray Data Collection and Structure Determination of 15. A crystal of **15** was obtained from a solution of CH_2Cl_2/EtOH. Oscillation and Weissenberg photographs indicated that the space group was triclinic. A hemisphere of intensity data were collected as above with unit cell parameters obtained by least-squares refinement of the orientation matrix with use of fifteen reflections in the range 10.9 < 2θ < 19.8° (Table IV) with positive 2θ measurements only. The three check reflections, remeasured after every 100 reflections, indicated no significant decay over the 89 h of data collection. Absorption corrections were deemed unnecessary. The data were reduced to F_o^2 as above,[10] with anomalous dispersion corrections included for Os. The atomic position of the Os atom was derived from the Patterson map. Subsequent Fourier and difference maps revealed all non-hydrogen atoms.

Several cycles of full-matrix least-squares refinement on all non-hydrogen parameters yielded R_F = 0.047, R_F' = 0.044, and GOF = 3.44;[22] final shift/errors < 0.10; and a data-to-parameter ratio = 11.0. All atomic coordinates as well as the scale factor, k, and Gaussian ellipsoids

Table IV. Summary of Data Collection and Refinement Information

	5	9	9′	15
formula	$C_{26}H_{18}OsN_4O_4Cl_4$	$C_{34}H_{32}OsN_4O_6Cl_4{\cdot}CH_2Cl_2$	$C_{34}H_{32}OsN_4O_6Cl_4$	$C_{20}H_{14}OsN_4O_4Cl_4{\cdot}^1/_2C_2H_6O$
formula wt	782.47	1009.60	924.67	920.42
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a, Å	10.083 (4)	19.907(6)	8.5333 (9)	10.860 (3)
b, Å	12.310 (5)	28.850 (7)	13.6879 (19)	12.633 (3)
c, Å	12.241 (4)	9.445 (3)	16.4148 (18)	12.844 (4)
α, deg	97.38 (3)	90	104.350 (13)	117.47 (2)
β, deg	96.49 (4)	131.79 (2)	97.329 (11)	90.42 (3)
γ, deg	113.0 (3)	90	79.179 (12)	95.90 (2)
v, Å^3	1364.7 (9)	4044 (2)	1817.8 (4)	1552.2 (7)
Z	2	4	2	2
D_{calcd}, g cm^{-3}	1.90	1.66	1.69	1.97
crystal size, mm	0.14 × 0.19 × 0.92	0.11 × 0.20 × 0.80	0.10 × 0.23 × 0.42	0.24 × 0.27 × 0.30
λ, Å	0.7107	0.7107	0.7107	0.7107
μ, mm^{-1}	5.11	3.60	3.86	4.68
scan type	θ–2θ	ω	θ–2θ	θ–2θ
2θ limits	$3 < 2\theta < 60°$	3–43°, 43–55°	4–30°, 25–56°	$4 < 2\theta < 40°$
scan rate, deg/min	2	6, 4	6, 2	2
scan width, deg	2.4	0.9	2.0	2.0
total collected refl	12429		9710	3283
final refl	6630	4657	8315	2915
refinement on	F^2	F	F^2	F^2
sec. extinction	3.9 (4) × 10^{-7}	5 × 10^{-5}		
final no. of parameters	353	264	442	264
final cycle [a]				
R_F	0.034 (6435)		0.051 (7989)	0.047 (2888)
R'_F	0.029 (5805)	0.031 (3903)	0.043 (6871)	0.044 (2710)
S	1.92 (6630)	1.60 (3903)	2.16 (8315)	3.44 (2915)

[a] The number of reflections contributing to sums given in parentheses; see ref 22 for definitions.

(anisotropic for all atoms except carbon and hydrogen) were in one block.

A difference map calculated after all non-hydrogen atoms have been located revealed the presence of additional electron density near a center of symmetry. This was measured to be an ethanol molecule with the two carbon atoms related by the center of symmetry and the two oxygen atoms disordered over two sites.

Hydrogen atoms were placed at a distance of 0.95 Å from their respective carbon or oxygen atoms by assuming ideal geometry and were not refined. The hydrogen atom temperature factors were set equal to the temperature factor of the atom to which they were attached.

Syntheses. All reactions were carried out in air unless otherwise noted. $K_2[Os(OH)_4(O)_2]$[24] and 3,5-dichloroacetylsalicylic acid[25] were prepared as described in the literature.

H_4CHBA-Et (1).[5] A 250-mL round-bottom flask with a stir bar was charged with 50.0 g (0.277 mol) of 2-acetylsalicylic acid and 50–60 mL of neat oxalyl chloride. The reaction flask was vented to a hood and maintained at 30 °C for 4 h. The remaining oxalyl chloride was distilled off in vacuo. The residue was dissolved in a 30-mL aliquot of CH_2Cl_2 which was also distilled off in vacuo; this step was repeated several times. A 500-mL round-bottom flask, equipped with a stir bar, was charged with a solution of 9.28 mL (0.138 mol) of ethylenediamine in 100 mL of CH_2Cl_2 and immersed in an ice bath. The acid chloride residue was dissolved in 100 mL of CH_2Cl_2, transferred to a dripping funnel and slowly added to the ethylenediamine solution with rapid stirring. The resulting slurry was stirred for 1 h. An excess of 1 equiv of triethylamine was added and the mixture stirred for an additional 0.5 h. This mixture was treated with ca. 100 mL of 6 M NaOH and heated in vacuo to remove the organic volatiles. The remaining aqueous solution was decanted from the undissolved organic residues which were then dissolved in a minimal amount of acetone and retreated with 6 M NaOH solution. All aqueous portions were combined and cautiously acidified with concentrated HCl. The precipitate was collected, washed with water, and recrystallized from acetone/water: yield 33.3 g (80%). Chlorination proceeded as follows: The unchlorinated product (5.0 g) was dissolved in 80–100 mL of glacial acetic acid in a 500-mL filtration flask. Chlorine gas was bubbled through the stirred solution for 0.5 h. The precipitated product was collected, washed with water, and recrystallized from acetone/water: yield 6.6 g (90%); ^{1}H NMR (Table I). Anal. Calcd for $C_{16}H_{12}Cl_4N_2O_4$: C, 43.87; H, 2.76; Cl, 32.37; N, 6.39. Found: C, 44.01; H, 2.81; Cl, 32.59; N, 6.36.

H_4CHBA-DCB (2).[5] 3,5-Dichloroacetylsalicyclic acid (12.55 g, 50.39 mmol) was converted to the acid chloride with 10–15 mL of neat oxalyl chloride according to the procedure described for **1**. 4,5-Dichloro-*o*-phenylenediamine (3.78 g, 21.35 mmol) was dissolved in 100 mL of CH_2Cl_2 and 15 mL of THF and cooled to 0 °C. The acid chloride was dissolved in 50 mL of CH_2Cl_2 and slowly added to the diamine solution. After the mixture was stirred for 1 h at 0 °C an excess of 1 equiv (12 mL) of triethylamine was added and the solution stirred for an additional 0.5 h at room temperature. This mixture was then treated with ca. 200 mL of 1 M NaOH and heated in vacuo to remove the organic volatiles. Ethanol was added to the resulting mixture until it became homogeneous. The solution was then slowly acidified with 1 M $HClO_4$. The precipitate was collected, washed with water, and recrystallized from THF/ethanol: yield 7.28 g (61%); ^{1}H NMR (Table I). Anal. Calcd for $C_{20}H_{10}Cl_4N_2O_4$: C, 43.28; H, 1.82; N, 5.05. Found: C, 43.34; H, 1.95; N, 5.00.

$K_2[Os(\eta^4$-CHBA-Et$)(O)_2]{\cdot}H_2O$ (3). Addition of a blue methanol solution of $K_2[Os(OH)_4(OH)_2]$ (0.500 g in 100 mL) to a colorless acetone solution containing 1 equiv of pure H_4CHBA-Et (0.595 g in 80 mL) produced an immediate color change to deep orange. The solution was stirred at room temperature for 10 min and then evaporated to dryness to give a quantitative yield of the product. Recrystallization of 200 mg from acetone/CH_2Cl_2 yielded 179 mg (90%) of orange microcrystalline product. After the sample was heated at 80 °C for 12 h under vacuum, NMR showed the presence of one H_2O per molecule of complex. On standing in air the compound reabsorbs ca. 3 additional molecules of H_2O per molecule of complex: Raman (aqueous) 870 cm^{-1} ($\nu_s(OsO_2)$); IR (Nujol) 820 cm^{-1} (v s, $\nu_{as}(OsO_2)$); ^{1}H NMR (Table I). Anal. Calcd for $C_{16}H_8Cl_4K_2N_2O_6Os{\cdot}(H_2O)$: C, 25.54; H, 1.34; N, 3.72. Found: C, 25.44; H, 1.50; N, 3.61. Incorporation of ^{18}O was effected by letting the compound stand with $H_2{}^{18}O$ for 24 h: IR (Nujol) 788 cm^{-1} (v s, ν_{as}-$(Os^{18}O_2)$).

$Os(\eta^4$-CHBA-Et$)(py)_2$ (5). $K_2[Os(\eta^4$-CHBA-Et$)(O)_2]{\cdot}(H_2O)_4$ (3) (0.540 g) was dissolved in 20 mL of pyridine and 15 mL of H_2O. Two equivalents of triphenylphosphine (0.356 g) in 15 mL of pyridine were added and the mixture was heated with stirring at 60 °C for 0.5 h. The reaction was accompanied by a color change to deep red-orange. The solution was evaporated to dryness and the residue warmed under vacuum for an additional 12 h to ensure complete removal of the solvents. The dry residue was washed with 20 mL of CH_2Cl_2 to remove the phosphines. The reduced intermediate, **4**, was collected as a red-brown solid which was then redissolved in 50 mL of THF and 10 mL of H_2O. To this solution was added 30% H_2O_2 (ca. 20 mL) in 20 mL of THF while cooling in a 0 °C bath. The solution was stirred at room temperature for ca. 15 min or until the color change to deep royal blue was complete. Addition of 20 mL of methanol followed by slow removal of the THF yielded 0.405 g (77% based on 3) of the deep blue crystalline product. An analytical sample was obtained by slow crystallization from THF/hexane: ^{1}H NMR (Figure 2) (Table I). Anal. Calcd for $C_{26}H_{18}Cl_4N_4O_4Os$: C, 39.91; H, 2.32; N, 7.16. Found: C, 39.93; H, 2.42; N, 7.14.

(24) Malin, J. M. *Inorg. Synth.* **1980**, *20*, 61.

(25) Durst, H. D.; Gokel, G. W. "Experimental Organic Chemistry"; McGraw-Hill: New York, 1980; p 256.

Os(η^4-CHBA-ethylene)(py)$_2$ (7).[5] Os(η^4-CHBA-Et)(py)$_2$ (**5**) (100 mg) was dissolved in 50 mL of THF and placed in a 250-mL round-bottom flask with 15 g of silica gel. The mixture was stirred and heated at reflux for 1 h and then evaporated to dryness. The dry silica was heated at 120 °C for 1 h and then placed on top of a small quantity of clean silica gel in a short column. Elution with CH_2Cl_2/acetone (4:1) removed the bulk of the product as a bright yellow band. Some starting material, **5**, and what appeared to be some of the corresponding Os(III) salt, **4**, remained on the column. Second and third fractions of the product were obtained by again heating the dry silica at 120 °C for 1 h and eluting on a short column as before. Filtration and removal of solvent from the combined fractions yielded the product as a dark gold-brown microcrystalline solid in >90% yield. An analytical sample was obtained by recrystallization from $CHCl_3$/hexane: ^1H and ^{13}C NMR (Tables I and II) (Figure 4). Anal. Calcd for $C_{26}H_{16}Cl_4N_4O_4Os$: C, 40.01; H, 2.07; N, 7.18. Found: C, 39.93; H, 2.10; N, 7.18.

Os(η^4-CHBA-*t*-1,2-diEtO-Et)(py)$_2$ (8a).[5] Os(η^4-CHBA-ethylene)(py)$_2$ (**7**) (100 mg) was dissolved in 20 mL of absolute ethanol and 20 mL of CH_2Cl_2. Addition of 90 mg of dichlorodicyanobenzoquinone (DDQ) caused an immediate color change to deep royal blue. After removal of the solvents by evaporation the product was extracted into CH_2Cl_2 and purified on a short silica gel column by elution with CH_2Cl_2/acetone (9:1). After recrystallization from CH_2Cl_2/pentane the product was obtained as a dark blue microcrystalline solid: yield 76 mg (68%); ^1H and ^{13}C NMR (Tables I and II). Anal. Calcd for $C_{30}H_{26}Cl_4N_4O_6Os$: C, 41.39; H, 3.01; N, 6.44. Found: C, 41.23; H, 2.96; N, 6.43.

Os(η^4-CHBA-*t*-1,2-diMeO-Et)(py)$_2$ (8b).[5] Os(η^4-CHBA-ethylene)(py)$_2$ (**7**) (100 mg) was dissolved in 20 mL of absolute methanol and 20 mL of CH_2Cl_2. The solution was treated with DDQ as for **8a** and the crude product was purified on two successive short silica gel columns. Recrystallization from CH_2Cl_2/pentane yielded the product as a dark blue powder. NMR established the structure of the product but also showed the presence of a small impurity (<10%). The impurity was separated from the product on a preparatory thin layer chromatography plate with CH_2Cl_2/THF (5:1). ^1H NMR indicated that the impurity was an asymmetrically substituted compound with one hydroxy and one methoxy group on the ligand bridge. This compound, **8°**, was the first in this series that had inequivalent NMR signals for the two pyridine ligands and for the two aromatic rings in the chelating ligand. It was therefore deliberately synthesized as discussed below. After removal of the impurity, the major product, **8b**, was again recrystallized from CH_2Cl_2/pentane: yield 43 mg (40%); ^1H NMR (Table I). Anal. Calcd for $C_{28}H_{22}Cl_4N_4O_6Os$: C, 39.92; H, 2.63; N, 6.65. Found: C, 39.94; H, 2.69; N, 6.61.

Os(η^4-CHBA-*t*-1-OH-2-MeO-Et)(py)$_2$ (8°).[5] Os(η^4-CHBA-ethylene)(py)$_2$ (**7**) (100 mg) was dissolved in 24 mL of CH_2Cl_2, 18 mL of absolute methanol and 3 mL of H_2O. The solution was oxidized with DDQ as for **8a** and **8b**. The reaction mixture was washed down a short silica gel column to separate out the quinones. TLC indicated that the crude product contained three blue compounds in the approximate ratio of 1:2:1. The three were separated on a preparatory thin layer chromatography plate with CH_2Cl_2/THF (4:1). One of the minor components was shown by NMR to be the dimethoxy-substituted compound **8b**. The major component proved to be the desired product, **8°**, and the other minor component was presumably the dihydroxy-substituted compound. The product was recrystallized from CH_2Cl_2/pentane and obtained as a dark blue microcrystalline solid: yield 35 mg (33%); ^1H NMR (Table I). Anal. Calcd for $C_{27}H_{20}Cl_4N_4O_6Os$: C, 39.14; H, 2.43; N, 6.76. Found: C, 38.97; H, 2.56; N, 6.55.

Os(η^2-Fo-CHBA)$_2$-*cis*-(py)$_2$ (9).[5] **Method a.** Os(η^4-CHBA-Et)(py)$_2$, (40 mg, 0.051 mmol) was dissolved in 25 mL of CH_2Cl_2 containing 0.1 M TBAP and 1 M of a 1° or 2° alcohol (methanol, *n*-butyl alcohol, isopropyl alcohol, or benzyl alcohol). The solution was electrolyzed in a three-compartment electrochemical cell at a BPG anode at +1.40 V vs. Ag/AgCl until the current had decayed to <5% of its initial value and TLC indicated that the reaction was complete. The anolyte was transferred to a beaker, and 65 mL of ether was slowly added. The precipitated TBAP was removed by filtration, and the solvents were evaporated from the filtrate. The resulting oil was dissolved in 25 mL of acetone, and the product was precipitated by addition of 50 mL of H_2O. The dark blue product was redissolved in CH_2Cl_2, dried over $MgSO_4$, and precipitated with hexane: yield 30 mg (72%). Anal. Calcd for $C_{26}H_{16}Cl_4N_4O_6Os$: C, 38.44; H, 1.99; N, 6.90. Found: C, 38.41; H, 2.06; N, 6.88.

Method b. Os(η^4-CHBA-ethylene)(py)$_2$ (**7**) (8 mg) was dissolved in 10 mL of CH_2Cl_2 containing 0.1 M TBAP and 0.5 M isopropyl alcohol. The solution was electrolyzed according to the procedure described in method a to give the desired product, **9**, and a trace of **9′**.

Several experiments were performed in which **9** was prepared from 1 mM **5** and 0.5 M benzyl alcohol and the product solution was analyzed by HPLC for benzyl ether. The HPLC analyses were performed on an IBM LC/9533 ternary gradient liquid chromatograph equipped with an octadecyl column and a 254-nm UV detector. The column was eluted with either ethanol/water (4:1) or isopropyl alcohol/water (3:2). Comparison of peak retention times with those of an authentic sample of benzyl ether indicated that in each case between 1 and 3 equiv of benzyl ether was detected.

Os(η^2-Fo-CHBA)$_2$-*trans*-(py)$_2$ (9′).[5] **Method a.** Os(η^4-CHBA-Et)(py)$_2$ (**5**) was oxidized by the same method used in the synthesis of **9** except that the CH_2Cl_2 contained 1 M *tert*-butyl alcohol or 1 M *tert*-amyl alcohol or was saturated with water; TLC indicated that the product was formed in high yield, but difficulty in purification and isolation produced a low yield (<30%) of the dark blue product: ^1H NMR (Table I). Anal. Calcd for $C_{26}H_{16}Cl_4N_4O_6Os$: C, 38.44; H, 1.99; N, 6.90. Found: C, 38.63; H, 2.16; N, 6.79.

Method b. Os(η^4-CHBA-Et)(py)$_2$ (**5**) (8 mg, 0.01 mmol) was dissolved in 10 mL of CH_2Cl_2 containing 0.5 M methanol and 2 M trifluoroacetic acid. To this solution was added a 0.1 M CH_2Cl_2 solution of tetrabutylammonium periodate which had been prepared from tetrabutylammonium hydroxide and periodic acid. TLC again indicated that **9′** was produced in high yield.

Os(η^4-CHBA-Et)(*t*-Bupy)$_2$ (5). $K_2[Os(\eta^4\text{-CHBA-Et})(O)_2]\cdot(H_2O)_4$ (**3**) (0.540 g) was dissolved in 15 mL of 4-*tert*-butylpyridine and 20 mL of H_2O. Triphenylphosphine (0.445 g, 2.5 equiv) was added to this inhomogeneous solution, and the resultant reaction mixture was treated as described for the unsubstituted pyridine adduct of **5**. This procedure yielded 0.505 g (84% based on **3**) of product as a dark blue microcrystalline solid. An analytical sample was obtained by purification on a preparatory TLC plate using CH_2Cl_2/THF (3:2) followed by recrystallization from CH_2Cl_2/pentane: ^1H NMR (Table I). Anal. Calcd for $C_{34}H_{34}Cl_4N_4O_4Os$: C, 45.54; H, 3.83; N, 6.26. Found: C, 45.56; H, 3.83; N, 6.23.

Os(η^4-CHBA-ethylene)(*t*-Bupy)$_2$ (7). Os(η^4-CHBA-Et)(*t*-Bupy)$_2$ (**5**) (100 mg) was heated on silica gel as described for the unsubstituted pyridine adduct of **7**. The product was removed from the silica as a bright yellow band by elution with CH_2Cl_2/acetone (9:1). Three fractions were collected as before and recrystallization from CH_2Cl_2 yielded the product as a very dark brown microcrystalline solid: yield 61 mg (61%). Anal. Calcd for $C_{34}H_{32}Cl_4N_4O_4Os$: C, 45.75; H, 3.61; N, 6.28. Found: C, 45.53; H, 3.63; N, 6.18.

Os(η^2-Fo-CHBA)-*cis*-(*t*-Bupy)$_2$ (9). Os(η^4-CHBA-Et)(*t*-Bupy)$_2$ (**5**) (50 mg, 0.050 mmol) was oxidized in the presence of methanol or isopropyl alcohol in the same manner used for the pyridine adduct of **9**. The product, which was isolated as before, contained significant amounts of the trans isomer, **9′**. The two compounds were separated on a preparative TLC plate (2000 μm, silica gel) by elution with CH_2Cl_2/THF (30:1). 32 mg (62%) of **9** was isolated as a dark blue powder from CH_2Cl_2/hexane. An analytical sample was obtained by slow crystallization from CH_2Cl_2/hexane: ^1H and ^{13}C NMR (Tables I and II). Anal. Calcd for $C_{34}H_{32}Cl_4N_4O_4Os$: C, 44.15; H, 3.49; N, 6.06. Found: C, 44.07; H, 3.68; N, 5.76.

Os(η^2-Fo-CHBA)-*trans*-(*t*-Bupy)$_2$ (9′). Method a. Os(η^4-CHBA-Et)(*t*-Bupy)$_2$ (**5**) (25 mg) was oxidized in the presence of 0.5 M *tert*-butyl alcohol with use of the same procedure as for the pyridine adducts of **9** and **9′**. TLC showed that the reaction was clean and that the product was formed in high yield. The high solubility of the dark blue compound led to a much lower yield of isolated material after recrystallization from boiling cyclohexane: yield 15 mg (58%); ^1H NMR (Table I). Anal. Calcd for $C_{34}H_{32}Cl_4N_4O_4Os$: C, 44.15; H, 3.49; N, 6.06. Found: C, 44.02; H, 3.53; N, 5.93.

Method b. Compound **9′** was formed as a minor product in the above synthesis of **9**. Ten milligrams (19%) of **9′** were recovered from the TLC separation of the two isomers.

$K_4[Os(\eta^4\text{-CHBA-DCB})(O)_2]$ (10). $K_4[Os(OH)_4(O)_2]$ (1.345 g, 3.65 mmol) was dissolved in 150 mL of warm methanol, and the solution was then bubbled with N_2 for 30 min. H_4CHBA-DCB (2.00 g, 3.60 mmol) was dissolved in 100 mL of THF and also bubbled with N_2 for 0.5 h. The blue osmate solution was added to the ligand solution at room temperature immediately producing the deep orange color indicative of product formation. The solution was stirred for 10 min under N_2 and then evaporated to dryness. The product was dissolved in a minimum of THF, filtered, and dried over molecular sieves. Addition of hexane followed by removal of THF yielded the product as a brown microcrystalline solid. NMR indicated the presence of 1.5 molecules of H_2O per molecule of complex: yield 2.620 g (86%); ^1H NMR (Table I); IR (Nujol) 820 cm^{-1} (v s, $\nu_{as}(OsO_2)$). Anal. Calcd for $C_{20}H_6Cl_6K_2N_2O_6Os\cdot1.5(H_2O)$: C, 27.40; H, 1.01; N, 3.20. Found: C, 27.60; H, 1.03; N, 3.19. Incorporation of ^{18}O was effected by dissolving the complex in dry THF, adding excess $H_2{}^{18}O$, and placing the solution under N_2 for 3 days: IR (Nujol)

782 cm^{-1} (v s, $\nu_{as}(Os^{18}O_2)$).

Os(η^4-CHBA-DCB)(PPh_3)$_2$ (11). To a 50-mL Erlenmeyer flask with a stir bar were added $K_2[Os(\eta^4\text{-CHBA-DCB})(O)_2]$ (**10**) (221 mg, 0.260 mmol), triphenylphosphine (450 mg), ca. 5 mL of trifluoroacetic acid, and 10 mL of THF. The orange solution was heated until most of the THF had evaporated and a dark green molten triphenylphosphine mixture remained (ca. 10 min). After cooling, the mixture was dissolved in 10 mL of CH_2Cl_2 and the solution was placed on a short silica gel column. Elution with CH_2Cl_2 removed the product as a green band. Addition of hexane followed by removal of CH_2Cl_2 yielded the product as a dark green crystalline solid: yield 236 mg (72%); ^1H NMR (Table I). Anal. Calcd for $C_{56}H_{36}Cl_6N_2O_4OsP_2$: C, 53.14; H, 2.87; N, 2.21. Found: C, 53.33; H, 2.94; N, 2.22.

Os(η^4-CHBA-DCB)(*t*-Bupy)(PPh_3) (12). Os(η^4-CHBA-DCB)-(PPh_3)$_2$ (**11**) (75 mg; 0.0593 mmol) was dissolved in 50 mL of CH_2Cl_2. Addition of 4-*tert*-butylpyridine followed by heating under reflux for 0.5 h produced a color change from dark green to light blue. Removal of solvents followed by recrystallization from CH_2Cl_2/hexane yielded the product as a dark blue crystalline solid. NMR showed the presence of 0.5 molecule of hexane per molecule of complex: yield 58 mg (86%); ^1H NMR (Table I). Anal. Calcd for $C_{47}H_{34}Cl_6N_3O_4OsP{\cdot}0.5(C_6H_{14})$: C, 50.82; H, 3.50; N, 3.56. Found: C, 50.72; H, 3.51; N, 3.53.

Os(η^4-CHBA-DCB)(*t*-Bupy)$_2$ (13). Os(η^4-CHBA-DCB)(PPh_3)$_2$ (**11**) (200 mg, 0.158 mmol) was dissolved in 20 mL of neat *t*-Bupy. The solution was heated under reflux for 15 min during which time the color changed from dark green to very dark blue, almost black. The *t*-Bupy was removed under vacuum and the crude product recrystallized from CH_2Cl_2/hexane. This yielded the pure product as a very dark crystalline solid. NMR showed the presence of 0.25 molecule of hexane per molecule of complex: yield 108 mg (68%); ^1H NMR (Table I). Anal. Calcd for $C_{38}H_{32}Cl_4N_4O_4Os{\cdot}0.25\ (C_6H_{14})$: C, 45.92; H, 3.46; N, 5.42. Found: C, 46.20; H, 3.52; N, 5.37.

Os(η^4-CHBA-DCB)(*t*-BuNC)$_2$ (14). $K_2[Os(\eta^4\text{-CHBA-DCB})(O_2)]$ (**10**) (120 mg, 0.135 mmol), triphenylphosphine (90 mg, 2.5 equiv), and *tert*-butyl isocyanide (0.20 mL, 12 equiv) were dissolved in 10 mL of THF and heated under reflux for 1.25 h. The solution was evaporated to dryness and the orange residue dissolved in CH_2Cl_2 and transferred to the top of a short silica gel column. The phosphine was removed by eluting with 300 mL of CH_2Cl_2, and the bright orange Os(III) intermediate was then removed with THF/acetone (1:1). This solution was concentrated and then treated with a dilute Br_2/THF solution at room temperature. The oxidation to the blue Os(IV) product was followed by TLC, and upon completion the reaction mixture was evaporated to dryness. The crude product was dissolved in 5 mL of CH_2Cl_2 and passed down a short silica gel column with CH_2Cl_2. Addition of hexane followed by removal of CH_2Cl_2 yielded the product as a dark blue crystalline solid: yield 20 mg (16%); ^1H NMR (Table I). Anal. Calcd for $C_{30}H_{24}Cl_4N_4O_4Os$: C, 39.71; H, 2.67; N, 6.17. Found: C, 39.75; H, 2.70; N, 6.19.

Os(η^4-CHBA-DCB)(bpy) (15). Os(η^4-CHBA-DCB)(PPh_3)$_2$ (**11**) (120 mg, 0.095 mmol) and bipyridine (210 mg, 1.34 mmol) were dissolved in toluene (10 mL) and heated under reflux for 0.5 h during which time the color darkened. The cooled solution was placed on a short silica gel column and eluted with excess CH_2Cl_2 to separate the product from starting material and 62 mg (78%) of product was isolated and recrystallized from CH_2Cl_2/hexane. Crystals for X-ray analysis were grown by vapor diffusion employing CH_2Cl_2/EtOH.

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Supplementary Material Available: Tables of data collection information, atom coordinates, Gaussian amplitudes, bond lengths and angles, and a listing of structure factor amplitudes (144 pages). Ordering information is given on any current masthead page.